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THE ACTION OF WATER ON LEAD.

Ernest Hart Esq

THE ACTION OF WATER ON LEAD

BEING AN INQUIRY INTO THE CAUSE AND MODE OF THE ACTION AND ITS PREVENTION.

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PREFACE.

The subject of lead poisoning from drinking water has lately attracted much attention, and it has been proved by the reports of Medical Officers of Health and others, that in certain districts a great danger to the health of the community exists in the form of lead in the water as supplied to the houses. Deaths from lead poisoning occasionally occur, and illness from the same cause is known to be widely prevalent in these particular districts. The lead is derived from the leaden pipes used to convey the water from the mains to the houses, and from leaden cisterns in which the water is sometimes stored. The water in the districts particularly affected is known to be of peculiar quality. It is generally obtained from moorland streams, and is a soft water with an acid reaction. The subsoil of the ground from which the water is drained consists of an insoluble rock, which is incapable of yielding any alkaline substance to the water, such as carbonate of lime, which would give the water an alkalinity. Hence it differs from water that has been in contact with any form of limestone, being devoid of carbonate of lime, and retaining its acidity. When such water is allowed to stand in a leaden pipe, it is found to take up a considerable quantity of lead, and this water being drunk habitually, is capable of producing a host of serious symptoms, individuals being affected by it in different ways.

The inquiries that have already been instituted in connection with the subject have elicited the fact that the exact chemical reasons for the action of water on lead are unknown, or at best but indifferently understood. An appreciation of this, gained by reading the more recent publications, was the stimulus which set the author to work upon the subject matter of the following pages. The record of the rather numerous experiments which will be found to constitute the bulk of the essay are set down fully as they are, in order to allow of repetition, and, if need be, correction by any chemist who cares to interest himself in the subject. Otherwise the author would apologize to his reader for so much minute detail and so many repetitions.

A proper understanding of the reason and mode of action of water on lead should enhance the possibility of preventing the action, and the labour has not been in vain if these experiments serve to let in only a little light which may enable other experimenters to arrive at fuller results.

STOKE NEWINGTON,
December, 1890.

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THE ACTION OF WATER ON LEAD.

I.—DISTILLED WATER.

THE action of distilled water on lead consists in the production of a solid white compound, said to contain a molecule each of hydrate and oxide of lead, its formula being Pb2HO, PbO. The solution of this compound in the water is a secondary and separate matter, which will receive notice in its place, but in the first place it is best to concentrate the attention upon the action which causes the production of this oxyhydrate.

If we look at the formula of the oxyhydrate, we see that it cannot be formed by the simple union of water and lead, but that every compound molecule requires what is equivalent to one molecule of water and two extra atoms of oxygen. There is only one method by which the oxyhydrate can be produced, if we consider the action to take place between lead and water alone, that is by displacement of hydrogen. Excepting at high temperatures, lead has not the reputation of displacing the hydrogen of water in the way that potassium, sodium, and some of the metals of the alkaline earths displace it, and it may be safely stated that if water *per se* has any action whatever on lead, it is so slow as to be of small importance. So we here are met at the outset by the crucial question: Whence, and in what manner, does the lead derive its oxygen?

The study of the action of water on lead is best begun with distilled water, because distilled water approaches most nearly to pure water. By the process of distillation it has been deprived of the greater portion of the solid constituents commonly found in ordinary natural waters. But distilled, or even redistilled, water is not absolutely pure. It contains a certain proportion of organic impurity, which is, at least in part, of nitrogenous composition. This organic matter must have been volatile originally, passing over with the water during distillation. It is very prone to decomposition, and forms a deposit in the water which contains it when the latter has been stored for any considerable length of time. If an ordinary distilled water be taken from the carboy in which it is stored, it may exhibit an apparent action upon lead, when placed in contact with that metal, or it may not. It will do so more often than not. Its action or non-action depends, as we shall try to prove further on, upon the condition of the organic impurity which it contains.

Experiments will now be given to illustrate the action of distilled water on lead, and the production of the solid crystalline oxyhydrate.

The lead used in this and in all the following experiments was a piece of new one-inch lead service pipe, which was cut into convenient lengths of about 1¼ inch, in order that the lead might be readily cleaned. Before each experiment, the pieces of lead were thoroughly scoured with a fine sand-paper, and afterwards rubbed with a soft bristle brush, and had the condition of perfectly clean white lustrous metal when dropped into the water. Most of the experiments were performed in jars of common white German glass, of about 12 ounces capacity. Five ounces of water and two pieces of lead were generally used, the water being sufficient to well cover the short lead tubes, one of which lay in the water with the axis of the tube horizontal, the other stood with the axis vertical. Excepting in the special experiments to be recorded, the air was freely admitted to the surface of the water.

Experiment I.—A distilled water placed in a glass jar, and two pieces of lead, prepared as above, dropped into it.

In less than ten minutes the action was observable, and after half-an-hour there was a small collection of white deposit on the bottom of the vessel, particularly round the piece of lead which was placed vertically, and from which the compound was evidently falling as it formed. On moving the jar a little cloud of white material was detached from the lead, which gave the water an opalescence. This was soonest seen inside the tube of lead that lay horizontal.

After 24 hours the bottom of the jar was everywhere covered with a layer of the white compound. About the sides and surfaces of the lead fine glistening crystalline scales were clinging, easily detached by a slight agitation. The water, which originally had been slightly acid to litmus, was now alkaline.

After 48 hours the action was still going on, more of the crystalline scales being produced.

After 96 hours the action was still progressing. The scales of white compound seemed to be larger than at first, but when shaken roughly were found to separate into smaller crystals, which had evidently been attached to one another. There was some slight amount of scum on the surface of the water. This action went on in the same way continuously through several weeks, until the lead was half buried in the deep layer of white oxyhydrate that had been produced. When the action had become well established, it appeared to proceed at a faster rate than at first, bulky masses of crystals forming rapidly on the lead. The jar being loosely covered by a piece of paper, a faint ammoniacal odour could after a time be detected in the air of the jar above the water, due, no doubt, to ammonia set free from ammonia salts, contained in the water, by the action of the lead hydrate upon them.

The action observed in this experiment is typical, and was obtained from several different distilled waters, as well as from certain other waters to be mentioned later.

The reaction of the water of this experiment was slightly acid to litmus to begin with, but the action was not due to the acidity of the water, for the very small amount of acid present was quickly neutralized, and during the remainder of the experiment the water was decidedly alkaline, the alkalinity being due to the basic compound of lead produced. Neither does the mere fact of an acid reaction appear to heighten the action in its initial stage, for distilled waters that were neutral or even very faintly alkaline from the first were found to act upon the lead with equal readiness. Nevertheless, those distilled waters which do not readily act on lead will be found to have an alkaline reaction.

Experiment II.—Another sample of distilled water (the reaction of which was alkaline to begin with) with lead in jar as before.

After one hour it was evident there was not to be the quick and decided action of Experiment I.

After 24 hours some rather large crystalline scales, or spicules, were formed, particularly upon the inner sides of the pieces of lead tube, being attached to the tube in patches. No lead compound on the bottom of the vessel.

After 48 hours crystals of comparatively large size, but few in number, lay at the bottom of the jar. The area of attack on the lead appeared increased, the adherent scabs of crystals covering a larger portion of the inner lining of the tubes. The outer sides of the tubes showed little sign of action.

After 72 hours the action was little, if at all, further increased. The outer sides of the lead tubes were scarcely affected.

Here we see a water that appears to have some power of action upon the lead, which action is apparently prevented, or at least retarded, presumably by something which is contained in the water, and which exercises an antagonistic influence, or obstruction, to the energetic action as exhibited in the water of Experiment I., and which this water also might exhibit were it freed from this obstructive influence. If this be a correct theory the study of the action of distilled water on lead resolves itself into two distinct sides, namely: 1. The cause of the action, and 2. The obstruction to the action.

Experiment III.—The distilled water as in Experiment I., which acted on lead with production of much oxyhydrate, was boiled in a glass vessel one minute. Its reaction, which had been previously acid, after boiling became decidedly alkaline, and being now placed in the jar with lead as before no action was apparent after several days.

In boiling this water one of two things must have occurred: either the destruction of the cause of action or development of obstruction to the action. It is quite a common thing for a water which acts on lead to lose its power of action when it is boiled in a flask, but it is not invariable, as shown in the next experiment.

Experiment IV.—A distilled water, which acted very strongly on lead in the way described under Experiment I., was boiled 10 minutes, then cooled and placed in the jar, lead being added. The reaction of the water was on the alkaline side of neutrality.

Action began quickly, and after one hour was marked.

After 12 hours a considerable amount of lead compound had been deposited on the bottom of the vessel and about the pieces of lead. It was of a curdy appearance.

After 48 hours much action had taken place; the product during latter part of time had been of the usual scaly crystalline appearance.

It is important to notice that the first portion of white lead compound produced had not the usual scaly appearance, but formed a more curd-like precipitate.

This experiment negatives the idea that when the action of a water is prevented by boiling the water, the destruction or dissipation of the cause of action is the true reason. On the other hand, the idea that the water contains a new substance after boiling in a glass flask which prevents the action being exercised receives accentuation. It is not improbable that the character of the organic material in the water may be altered by boiling, and a compound be formed capable of coating the lead by giving up CO_2 which would be utilized to form a basic carbonate upon the surface of the metal. The increase of alkalinity observed in a water after boiling in a glass vessel may, however, be due to solution of alkali from the glass, and that this is the more likely hypothesis is proved when we find the alkalinity not increased after boiling the same water in a platinum vessel. In the latter instance it remains an open question whether the obstruction is due to silica or to carbonate of soda. In Experiment IV. we may suppose there was not sufficient of this obstruction produced from either cause to stop the action, but enough to modify the first portion of the product, which had an unusual curdy appearance. In Experiment III., which was a different sample of distilled water, there was enough produced on boiling to completely stop the action. It is very likely also that the imperfect action exhibited by the water of Experiment II. arose from the same cause, that is, from the fact of the water containing a substance capable of giving the lead an insoluble coat. We saw that the parts of the lead most affected were on the inner sides of the tubes; that is to say, the parts most remote from the influence of the bulk of the water. It was noticed also in numerous experiments, both with distilled and other waters, in which a protective influence was exercised, that a very little action with production of solid white lead-salt occurred on the under surface of the piece of lead pipe that lay horizontal close to where it touched the glass, and also on the piece of lead pipe which stood vertical, where it leaned against the side of the jar. Where the lead was in actual contact with the glass it retained its original polish as a roundish or oval bright spot, the remainder of the surface being covered with a darker coat. At the line of junction of the bright and darkened part a little white lead compound was produced. When this is seen to happen it may be taken as a sign that the protective influence in that water is not very powerful. When the action of the water on the lead is patchy, that is when some parts of the lead are acted upon and some escape, the indication is not that the tendency is for the action to take place from certain points or centres owing to some physical condition of the metal, or from galvanic action, a view which seems to be entertained by the author of a recent publication, but merely that the lead is protected in those parts where action does not occur, the protective influence—generally carbonate—not being sufficient to cover the whole. The likelihood is great that, at least after being kept a few days, all ordinary distilled waters, as well as most natural waters, possess power of acting on lead to produce the oxyhydrate, but the exercise of this power is in many instances prevented by the power that waters at the same time possess of giving the lead an insoluble coat, a power which we have termed "the obstruction." In the case of distilled waters, this obstruction is not great in amount, and therefore not difficult to remove, an obvious method of removing it being to remove the lead upon which it has exhausted itself. Thus, suppose there be no production of the oxyhydrate of lead in an experiment with a distilled water, that is of alkaline reaction, at the end of a few hours let the lead be removed from the water, cleaned and replaced, or substituted by fresh clean pieces of lead. Often in the case of distilled water, when the surface of the lead exposed to the action bears the proportion to the volume of water as in the above experiments, one change of lead will be found sufficient, but if action is not then set up, the obstruction in the water being still sufficient to cover the lead with a protective coat, the lead may be changed again and again until action at last ensues, when all the obstruction is withdrawn, as it certainly can be by this method.

Experiment V.—A distilled water which acted strongly on lead with production of oxyhydrate was placed in a glass jar, and so much solution of carbonate of ammonia dropped in from a burette as to give it a strength equal to one grain $Am_2 CO_3$ per gallon. The lead was then put in.

Action began quickly and proceeded for a short time sluggishly, and was then checked.

After 24 hours it was evident the carbonate had stopped the action, which at first took place so rapidly that a little lead compound was produced and detached from the lead before sufficient carbonato of lead could be formed to cover the metal.

After 48 hours no further action had taken place.

The lead was now removed, cleaned thoroughly by scouring with sand paper and brushing with a soft brush, and returned to the water.

Action commenced immediately, and the remaining carbonate of ammonia was insufficient to again stop it, but in six hours the lead remained uncoated and a considerable amount of compound had been produced. It was of a curdy appearance.

After 24 hours much action had taken place, as much, to all appearance, as if the carbonate of ammonia had not been added. The action afterwards went on continuously, the after-product consisting of the usual crystalline scales.

Experiment VI.—A distilled water which acted strongly on lead with production of oxyhydrate was well shaken with precipitated chalk in such proportion that if all the chalk had been dissolved the strength would have been equal to three grains of $Ca CO_3$ in the gallon. But very little was dissolved, certainly not one-third of the above quantity. The water was then separated from excess of chalk by filtration through filter paper, and the usual two pieces of lead were put into it.

After 24 hours a very trifling amount of action had taken place, the product being of a curdy appearance.

After 48 hours a very little more action had occurred. The tubes were lined with adherent lead-salt and marked with patches of the same externally. There was a very little curdy deposit at the bottom of the vessel.

After 96 hours the action was stationary, and the result therefore was that the very small quantity of carbonate of calcium in solution had not been able to immediately stop the action of this strongly acting water, but during the first two days had greatly retarded it and had finally stopped it completely.

The lead was now taken out, cleaned and returned, and it was then discovered that the carbonic radicle had been so far removed that the action was now as rapid and continuous as in the original water.

Experiment VII.—Water distilled from a glass retort. It was the first that came over, and besides containing the "free ammonia" of the original water, it contained some splashings. The water in the retort was that of the New River Company containing about 13 grains $Ca\,CO_3$ per gallon.

The distilled water was filtered through paper and put into the glass jar with lead in the usual way. Its reaction was decidedly alkaline.

After 24 hours a very slight action had taken place upon the inner surfaces of the lead pipes only. The outer surfaces were only darkened.

After 48 hours no further action had taken place. Where the lead was protected from the main bulk of the water, as near to where it touched the glass, there was a little deposit of white lead-salt, and it was thus made evident that the water contained both the cause of the action and the obstruction to the same.

The lead was now taken out, dried, scoured, polished, and returned.

After 12 hours a considerable quantity of curdy deposit had been produced upon the lead and upon the bottom of the jar.

It has been before hinted that when the product is of this curdy nature the presence of carbonate is betokened. The carbonate, however, is not present in sufficient quantity to stop the action by rapidly converting the very first portion of oxyhydrate produced into an insoluble carbonate of lead, which, attaching itself closely to the surface of the metal, protects it from the further action of the water.

From the consideration of the obstruction to the action of distilled water on lead let us now pass to the consideration of the cause of the action. The following experiment proves that the supply of oxygen is not gained by the decomposition of water with evolution of hydrogen :—

Experiment VIII.—A distilled water which acted strongly on lead, in the usual way, with production of crystalline oxyhydrate, was placed in a glass basin which was so deep that a small glass beaker, when introduced sideways, was completely submerged. The beaker being then inverted remained perfectly full of water, and a piece of cleaned lead being introduced beneath its mouth, the beaker was allowed to stand over it so that any hydrogen evolved would displace the water and be collected at the top of the beaker.

The action of the water began immediately, and after 24 hours a little heap of white compound lay all round the lead within the beaker.

After 48 hours more of the oxyhydrate had been produced, but not the smallest bubble of gas had been collected at the top of the beaker.

After 96 hours the action had apparently come to a standstill. After 144 hours the lead-salt was very slightly, if any further, increased, and there was no gas in the beaker.

The beaker was now removed, and the water it had enclosed was consequently mixed with the bulk of the water in the basin, and fresh water being brought into contact with the lead, the result was that the action commenced again immediately.

From this experiment we learn two things. In the first place no hydrogen is evolved. In the second place, when the water about the lead is limited, and the air cut off, the action, with production of oxyhydrate, is not interminable, but proceeds for a comparatively short period only, and then comes to an abrupt end.

So we must put aside the idea that the lead decomposes the water displacing hydrogen, and appropriating oxygen and hydroxyl to form the compound Pb2HO, PbO, and we infer from our last experiment that water contains oxygen in another form than in combination as water; that it is from this oxygen the lead draws its first supply, and that the after-supply is drawn from the air when we see the action continued through many days or weeks, as in Experiment I.

In Experiment VIII. the mouth of the beaker did not fit so closely down upon the bottom of the basin as to make a complete separation between the water inside the beaker and that outside it;

but if any currents were established between the water inside the beaker and that outside it, the interchange of water must have been very slow. The effect of cutting off the air, however, was exemplified in a more perfect manner in the next experiments performed simultaneously for the object of comparison.

Experiment IX.—A distilled water that acted strongly on lead placed in a glass jar and lead put in precisely as before, the air being allowed free admission to the water.

Experiment X.—The conditions were exactly as in Experiment IX., but melted hard paraffin was poured on the surface of the water to a depth of half-an-inch, and by this means the air was excluded.

After 24 hours. A considerable and apparently equal amount of action had occurred in both jars, the bottoms of the jars being covered with deposit of white lead oxyhydrate, the apparent amount and character of the lead-salt being the same in both jars. Three or four large bubbles of gas were visible under the paraffin of Experiment X.

After 48 hours. In Experiment IX. the action had increased, and the product was greater in amount than at this time observed in Experiment X. In the latter experiment some more lead oxyhydrate had been produced, but the action had been slower, and the total amount of lead salt was now not so great as in Experiment IX.

After 72 hours. In Experiment IX. the action appeared to be going on faster than ever; but in Experiment X. there had been little, if any, further production of oxyhydrate.

After 120 hours. In Experiment IX. the action was continuing, the oxyhydrate produced being now greatly in excess of that produced in Experiment X. In the latter experiment the action had apparently ceased. There were still gas bubbles under the paraffin, but they were (?) smaller than when first noticed.

The paraffin was now removed with a knife, and the pieces of lead pipe removed from both waters. The solid oxyhydrate that had been produced was then dissolved by adding to each jar a few drops of hydrochloric acid, and the lead in each jar was estimated. The five ounces of water of Experiment IX. contained $1\frac{1}{6}$ grain of lead (Pb). The five ounces of Experiment X. contained $\frac{1}{4}$ grain of lead.

The occurrence of gas bubbles under the paraffin looks on the face of it as if gas had been evolved as the outcome of the action. The presence of these bubbles, however, admits of a better explanation. The paraffin is, of course, warm when it is poured on to the water. Where it touches the sides of the glass jar it adheres firmly and sets quickly, but the chief mass of the paraffin solidifies more slowly and contracts, and in consequence it is, in a measure, lifted up from the surface of the water, and the result is a vacuum or several small vacua between the paraffin and the surface of the water. The gases dissolved in the water rise into these vacua and form the air bubbles. That the lead has nothing to do with their production can be easily proved by repeating the experiment without the lead, in which case the bubbles will be found to occur as before.

Experiment X. supplements Experiment VIII. in proving that the water contains oxygen free or combined, which is applicable, so far as it goes, to the production of oxyhydrate from metallic lead when the latter is placed in contact with the water. The indefinite continuation of the action, however, requires the free admission of air from which a never-failing supply of oxygen can be obtained.

We have seen that in the case of many distilled waters the action was prevented on boiling them in glass vessels, and have proved that the reason it was stopped was not on account of the destruction of the cause of action, but on account of the development of an obstruction to that action which it was possible to remove. In Experiment IV. we had a water in which this obstruction developed after boiling ten minutes, was not sufficient to stop the action of the water on the lead, presumably owing to the fact of the water containing too little of the organic material from which the obstruction may be, in part, produced upon boiling, or to some other unnoticed circumstance. In this experiment the gases dissolved in the water must have been dissipated. True, on cooling down the water, the gases of the atmosphere would, in the course of time, be reabsorbed, and the assertion that free oxygen, dissolved in the water, is not the cause of the action, might, in consequence, be called in question. But the action observed when lead was put into this recently-boiled water was so immediate and decided as to render it improbable that it was due to dissolved free oxygen, and in an experiment to be mentioned hereafter with a water similar in character with that of Experiment IV., considerable action was found to take place at 212° F. Therefore, we may take it that the lead derives its first oxygen from another source than that of free O_2 dissolved in the water. The same argument holds good for any other gas that is merely dissolved in the water. If we next direct our attention to a list of the compounds which waters of one sort and another are known to hold in solution, the presence of the nitric radicle, existing in the form of nitrates, must strike us as a very likely source of oxygen from which the oxyhydrate of lead may be formed.

That the presence of added nitrate has effect in overcoming slight obstruction in a water is proved by the experiments which follow. From them also some information may be gained of the general effect of nitrate when contained in water in considerable proportion.

Experiment XI.—A distilled water of slightly-alkaline reaction, similar to that of Experiment II., in which the action on the lead was obstructed, was made to contain three grains of nitrate of ammonia in the five ounces of water. Lead was then put into it as before.

Action commenced immediately and went on slowly and continuously. The lead-salt produced had a different appearance to that produced by distilled water alone. It consisted of fine separate crystals, which, when shaken up, gave the water a silky or micaceous appearance.

After 72 hours, action was continuing, but apparently more slowly than in the case of a strongly-acting distilled water.

Half-an-hour after the commencement of the action the water was tested for nitrite, which was readily discovered. A considerable scum developed on the surface of the water of this experiment, consisting of crystals of a salt of lead. The water contained a very appreciable quantity of lead in solution.

Experiment XII.—A distilled water that, alone, had a slight patchy action on lead, evidently containing some small amount of obstruction, had half a grain of nitrate of potassium dissolved in the five ounces contained in a glass jar, and clean lead was then dropped in as before.

After 24 hours the bottom of the jar was covered with a layer of fine white compound, the lead tubes being also partly covered with the same.

After 72 hours much more of the lead compound had been produced.

The action continued for several more days and then came to a termination, and, though the jar was kept for several weeks, no further action took place. No scum whatever was developed on the surface of this water, and the appearance of the white product was not like that obtained with nitrate of ammonia as in the last experiment, and quite unlike that obtained by the action of plain distilled water, but had a dense pulverulent appearance. The supernatant water yielded copiously of nitrites, but contained no lead in solution.

Experiment XIII.—The same distilled water as in the last experiment, but containing five grains KNO_3 in the five ounces, with lead as before.

After 24 hours slight action had occurred, not nearly so marked as in Experiment XII. in the same time.

After 72 hours the lead salt produced had been a little increased in quantity, but was far less than that produced in Experiment XII. in the same time. Under the piece of lead that lay horizontal a portion of the compound produced was of a yellow colour.

Experiment XIV.—The same distilled water as in the last two experiments, but made to contain 50 grains KNO_3 in the five ounces, with lead as before.

After 72 hours the apparent effect was much less even than in Experiment XIII. The lead was merely covered with a thin coat of white compound. The water contained no lead in solution.

In these, and in other experiments, the addition of nitrate of ammonia or nitrate of potassium set up action where otherwise there would have been none or next to none. When nitrate of ammonia was added to the water in such large proportion as three grains in five ounces, the lead-salt produced had a different appearance and probably a different constitution to that which occurred as the result of the action of a distilled water alone.

If a mere trace of nitrate of ammonia be added to a distilled water, the action may at first be modified, the lead-salt produced being different in appearance, but if the action be allowed to go on for many days, the appearance of the ultimate product is the same as that produced by a distilled water alone. The difference observed when a good deal of nitrate is present may be due to the first portion of lead-salt produced being a basic nitrite, and when the water previously contained obstruction also in part a basic carbonate in place of the usual oxyhydrate.

In Experiment XII., with half a grain of KNO_3 in the five ounces of water, the ordinary action of a distilled water is clearly superseded by another action which appears to go on just as long as it can draw material from the nitrate and then comes to an end.

An increase in the strength of the solution of nitrate of potassium leads to a diminution of the lead-salt produced. Thus we see with so strong a solution as 50 grains in five ounces, the only effect produced is a thin coating on the lead of an insoluble lead compound, which will, on account of its covering the lead, protect the metal from the further oxidizing action of the excess of nitrate of potassium in the water.

Mention has been made of a scum which is seen upon the surface of the water in most of the experiments. Sometimes it is considerable, sometimes very slight. Where much lead exists in solution, as in the water to which nitrate of ammonia has been added, the scum is thick. In the water containing nitrate of potassium, where there is no lead in solution, there is no vestige of scum. The scum contains crystals of lead-salt—carbonate of lead, no doubt—and is formed upon water containing lead in alkaline solution on exposure to air—a result, in fact, precisely analogous to what takes place when lime-water is exposed to air. There is formation of a pellicle of carbonate of calcium on the surface, due to absorption of carbonic acid gas from the air. The occurrence of such a scum upon the surface of a water that has been in contact with lead is a sign that lead is dissolved in the water, and that the solution is alkaline. In the case of distilled water, the scum is very thin, often not enough to cover the whole surface, but in waters containing much ammonia-salt it is always considerable.

Experiments XV., XVI., and XVII.—The water used in these experiments was a distilled water of slightly alkaline reaction, that, alone, had but a limited patchy action on lead. The three experiments were done simultaneously.

In Experiment XV. the five ounces of water had dissolved in it half a grain $AmNO_3$.

In Experiment XVI. the five ounces contained $\frac{1}{8}$ grain $AmNO_3$.

In Experiment XVII. the five ounces contained $\frac{1}{16}$ grain $AmNO_3$.

Action soon commenced in all with production of white compound of lead. At first the product appeared greatest in amount in the jar which contained least $AmNO_3$ and least in that which contained most of the ammonia nitrate, and even to the end of the experiment a difference was noticeable; it still appeared greater where there was least ammonia nitrate, but the crystals were smaller, more distinct from one another, and formed a more dense precipitate in the jars containing most ammonia-salt.

After 96 hours the pieces of lead were removed from the respective jars and the lead dissolved in the water of each jar estimated in the water after filtration through paper. The solid product being caught on the filters was, in each case, dried equally with the others and weighed. That derived from the water containing least $AmNO_3$ was more bulky than the others, and it lost most weight in drying. The weight of the dry lead-salt was, in each case, within a small fraction of six grains, so that the addition of a larger or smaller quantity of $AmNO_3$ had had little effect in increasing or diminishing the oxidation of the lead, the difference as appreciated by the eye being probably due only to the molecular combination of water with the lead-salt. The amount of lead actually dissolved in the water, however, showed a marked difference, being directly proportionate to the ammonia-salt present.

Table showing the effect of different quantities of nitrate of ammonia in a distilled water in regard to the production of solid lead compound and its after solution in the water.

Water 5 oz.	Lead in solution after 96 hours.	Solid lead compound produced in 96 hours.
Containing—		
$\frac{1}{16}$ gr. Nitrate of Ammonia.	$\frac{1}{3}$ gr. per gallon.	6 grs. in the 5 oz.
$\frac{1}{8}$,, ,, ,,	3 ,, ,,	6 ,, ,,
$\frac{1}{2}$,, ,, ,,	8 ,, ,,	6 ,, ,,

In the following experiments we get corroboration of the same thing with a different water, and when much smaller quantities of nitrate are employed.

Experiments XVIII., XIX., XX., and XXI.—The water was a redistilled water that had been kept a short time, five ounces being used in each case, and lead dropped into the respective jars as before. The four experiments were simultaneously performed.

In Experiment XVIII. the water contained no added nitrate.

In Experiment XIX. ammonia nitrate was added, the strength of the solution being equivalent to $\frac{1}{5}$ grain $AmNO_3$ per gallon.

In Experiment XX. the strength of the solution equalled $\frac{3}{5}$ grain $AmNO_3$ per gallon.

In Experiment XXI. the strength equalled one grain per gallon.

The action in each of these experiments was comparatively slow, and after 72 hours the apparent amount of solid lead-salt produced was about equal in each jar.

The lead was now romoved from each jar, and a portion of the supernatant water of each experiment was filtered through paper, and the lead in solution estimated in each. Afterwards, a few drops of hydrochloric acid being added to the remaining water in each jar, the solid lead-salt was dissolved, and was estimated also by the colorimetric method with sulphuretted hydrogen. The approximate result was as in the following table.

Table showing effect of different quantities of nitrate of ammonia, when added in very small proportion to a distilled water, in regard to the production of solid lead compound and its after solution in the water.

Water 5 oz.	Lead in solution at end of 72 hours.	Lead existing as solid lead-salt produced in 72 hours.
Redistilled water alone.	$\frac{1}{80}$ grain per gal.	1 grain in the 5 oz.
Redistilled water containing—		
$\frac{1}{3}$ gr. per gal. $AmNO_3$	$\frac{1}{10}$ " "	1 " "
$\frac{3}{5}$ " "	$\frac{1}{5}$ " "	1 " "
1 " "	$\frac{1}{2}$ " "	1 " "

These experiments teach that the addition of nitrate of ammonia to a water that already possesses power of acting on lead with production of solid oxyhydrate, does not enable the water to act more quickly and produce a greater amount of oxyhydrate in a given time. If anything, the evidence is to the contrary, proving that when a very large proportion of nitrate is present the ordinary action with production of solid oxyhydrate is retarded, the one process being substituted by another. The addition of nitrate of ammonia, however, affects the solution of the lead compound in the water to a marked degree, the amount dissolved being proportionate to the nitrate of ammonia present. The addition of nitrate, moreover, at least when the nitrate is considerable in quantity, causes any slight obstruction to be overcome, though it cannot cause action in a water that is strongly protected, such as a comparatively hard water, *e.g.*, that of the New River Company, which contains about 13 grains of carbonate of calcium per gallon, as was ascertained by experiment.

On the other hand, the idea of the action of water on lead being due to the presence of nitrate in the water is not contradicted by these experiments. The amount of nitrate naturally contained in distilled water is often infinitesimal, and an infinitely small proportion of nitrate may be sufficient for gradual operation, if we consider the process to be one of continued deoxidation of the nitrate by the lead, and its reoxidation by the oxygen derived from the air. In this case also it is very natural to suppose that the oxyhydrate of lead produced would be less compact, and have a higher degree of hydration, would fall from the surface of the lead, as it is produced, more readily, and would consist more entirely of simple oxyhydrate rather than of a basic salt, containing nitric oxide or nitric peroxide. All these are points of importance in the consideration of the experiments that have yet to be recorded.

Lead, and also copper, when placed in a solution of any common nitrate, including nitrate of lead itself, rapidly causes reduction of the nitrate or a part of it, and nitrite occurs in the solution, oxide of lead being at the same time formed. In any of the foregoing experiments, in which nitrate was added to the water, nitrite could be detected in a very short time, and after a few hours the water gave a very copious reaction for nitrite in each case when the starch, iodide, and acetic acid test was applied. The fact that lead does thus reduce nitrate to nitrite, even in the weakest solutions, must be accepted as strong *primâ facie* evidence in favour of nitrate being the source from which the first supply of oxygen is derived by the lead. Naturally, a contemplation of this fact led to each of the distilled waters being tested for nitrite after they had exhibited their action upon lead, and the supernatant water in every one of the experiments, where plain distilled water had acted with production of oxyhydrate, yielded a slight reaction for nitrite when the reagents were applied in the most careful manner, a little time being, however, sometimes required for the full development of the violet colour obtained, whereas generally in the original waters no such reaction could be obtained. We do not possess any test for nitrate so delicate as our test for nitrite, but when any of these waters in their original condition were evaporated down with a trace of pure caustic soda the residue gave in each case a considerable coloration with brucine and sulphuric acid, denoting the presence in the water of traces of nitrate.

The discovery of nitrite in the water after contact with lead, backed by the circumstantial evidence which follows, proves that when a distilled water acts upon lead to produce oxyhydrate, the oxidation of the lead is brought about through the mediation of the oxides of nitrogen, in combination as nitrites, etc., which act between the air and the lead as oxygen carriers.

When the pieces of lead which have been exposed to the action of the water are removed, and allowed to dry in the air, they are seen to be covered either with a thin iridescent film in cases where the water contains obstruction, and the lead is consequently protected from its action, or a white coat, somewhat resembling the bloom which occurs on fruit, and which can generally be wiped off with ease, in cases where the lead is entering into solution, or where slightly soluble solid basic salt has been produced. When a drop of dilute sulphuric acid is dropped on to a piece of lead with this fur or bloom upon it, a slight but decided nitrous odour can be detected when the lead is raised to the nose. Drops of solution of iodide of potassium and starch being now also dropped upon the lead, the blue coloration is very plainly developed. The lead removed from the jars where oxyhydrate was being produced by action of distilled water gave these signs of nitrite at its surface.* The nitrous odour obtained does away with any doubt as to the possibility of the iodine in the test being set free by another means. Next the white compound itself, which we have called oxyhydrate, effervesces slightly when sulphuric acid is added to it, and sometimes the nitrous odour can be detected in the gases evolved. The effervescence is due to evolution of one or more of the oxides of nitrogen, together with carbonic acid gas, because what little carbonic acid gas was originally contained in the water, free or combined, may now be expected to exist in combination with oxide of lead as basic carbonate. When the oxyhydrate is exposed to the air in a moist state more CO_2 is rapily absorbed, and the effervescence, on adding an acid, thereby increased. With sulphuric acid starch and iodide of potassium, the "oxyhydrate" gives the reaction of nitrite. This is more plainly obtained here, as also at the surface of the lead, with sulphuric acid than with acetic acid, owing to yellow iodide of lead being formed with the latter acid, which rather mars the result. A dirty green colour, however, is obtained when acetic acid is used.

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* When ordinary sulphuric acid is dropped upon perfectly clean lead some evidence of nitrite can generally afterwards be detected, it being derived from nitric acid, contained as an impurity in the sulphuric acid. Cognizance was taken of this, and allowance made in the experiment with lead removed from distilled water.

Now, supposing the water to contain a minute quantity of nitrate of ammonia to begin with. The lead reduces this to nitrite, and hydrate of lead is formed. This hydrate of lead at once decomposes the nitrite of ammonia, and nitrite of lead and hydrate of ammonia exist in the solution (see Experiment I., where odour of ammonia was developed in the loosely covered jar). Further action, we may suppose, is between the lead and the lead nitrite, the latter being continually oxidized into nitrate by oxygen absorbed from the air, and reduced again to nitrite at the surface of the lead. Or the deoxidation may go a step further, and the nitrite become reduced to hyponitrite, and further action be due to the continual oxidation of hyponitrite to nitrite, and reduction back to hyponitrite, which never again reaches the state of nitrate until the water be used up. One other, and probably the most likely alternative, is that the nitrogen exists in several, let us say three, conditions of oxidation at one and the same time. That the lead has power not only of reducing nitrate to nitrite, but of further reducing the nitrite, admits of proof, as in the following experiment. In Experiment X., in which the air was excluded by paraffin, it had been noticed that when the paraffin was removed and the water tested for nitrite the colour was a long time appearing.

Experiment XXII.—A distilled water that acted strongly had lead placed in it, and was then covered with paraffin, as in Experiment X.

After three or four days, when the action had some time come to an end, the paraffin was removed, the lead taken out, and the water divided into two equal portions. Starch, iodide of potassium and sulphuric acid being added equally to each, the one was left open to the air, the other was immediately covered and protected from the air, by pouring on its surface olive oil to a depth of half-an-inch. After some hours the violet colour gradually appeared in the water, to which free admission of air was given, but no colour had developed in the water covered with oil after many days.

Thus when the supply of air is cut off, lead uses up all the available oxygen, reducing nitrate to nitrite, and nitrite to a compound of lower oxidation. Through the medium of the nitrogen oxides, it also removes all the free oxygen contained in the water.

The actual quantity of nitrate or nitrite required to be present in order that action may occur, in the absence of obstruction in the shape of carbonate, etc., is extremely small.

The origin of the nitrogen oxides in distilled waters may be sought in the decomposition of the organic material which such waters invariably contain. If a water, immediately after distillation, is found to have an action on lead with production of oxyhydrate, the action may be due to a trace of nitrate of ammonia, which either had existence in the water previous to distillation, or was produced upon boiling it. Stale distilled waters, in which a deposit of flocculent matter has occurred, generally exhibit the strongest power of action. They may, however, contain obstruction which has to be removed with repeated change of lead before any considerable continuous action can take place. A distilled water which on one day is active, may have lost its power—that is, have developed obstruction—a week later. On the other hand, a distilled water which at first exhibits slight action or none may, within a few hours, have acquired the requisite power for the rapid production of oxyhydrate of lead. The influences of light, heat, exposure to air, etc., which cause these differences, have yet to be studied, as well as the influence of the micro-organisms, which undoubtedly occur in stale distilled waters in very considerable number and variety. It is not difficult to form theories upon the matter in absence of positive proofs. To suppose that one variety of organism, say a bacillus, causes the breaking down of the organic matter as it occurs in the first place, and that carbonate of ammonia is one of the products. In connection with our subject, let us call this the obstructive process. Another organism, say a micrococcus or an oïdium, causes the oxidation of the carbonate of ammonia, producing the cause of the action of water on lead, at the same time destroying the obstruction. What the composition of all the products of oxidation may be is but a matter of conjecture. That the change from carbonate to nitrite of ammonia takes place at one leap does not commend itself as likely, and there may be, and probably are, products of intermediate constitution, compounds containing nitric oxide and nitric peroxide, not in combination as acid radicles, but rather as substitution molecules, which readily part with an atom of oxygen to lead, and acquire a fresh atom from the air. Such compounds, if they exist, must be included in the oxidized nitrogen to which the action of water on lead is due.

The whole process of nitrification requires further study and elucidation.

The next experiment is very suggestive of bacterial influence. A rough cultivation of the bacteria in a drop of one of the distilled waters which acted strongly on lead was made in nutrient gelatine, and used as below.

Experiment XXIII.—A freshly-distilled water that acted slightly and slowly on lead, with production of oxyhydrate, had added to it one drop of the liquefied gelatine of the above cultivation. It was then placed in a water bath, and kept at a temperature of 105° F. for 24 hours.

The first effect of adding the drop of liquefied gelatine was greatly to increase the "free ammonia" in the water, but neither the water nor the liquefaction of the bacterial cultivation itself gave evidence of containing nitrite; neither did the liquefied gelatine contain any appreciable nitrate.

After the water had been heated four hours it was tested for nitrite, which was present in it.

After 12 hours no nitrite could be discovered.

After 24 hours no reaction for the nitrite was obtained. The nitrate in the water, as tested for by brucine and sulphuric acid, was markedly increased. The "free ammonia" was diminished.

The water was now allowed to get cold, and lead was placed in it in the manner before described.

Experiment XXIV.—The same water as in Experiment XXIII., with one drop of the same liquefied nutrient gelatine added, and lead immediately put in without any previous warming.

In Experiment XXIII. the production of solid lead-salt was apparently faster from the first than in Experiment XXIV. In both the experiments the product was similar to that obtained when nitrate of ammonia is added to water, the crystals being fine and distinct, but at the end of 72 hours in Experiment XXIII. the crystals were becoming more aggregated, and similar to those that occur in the case of an ordinary strongly-acting distilled water.

At the end of 72 hours the lead was withdrawn from both waters, the solid lead-salt dissolved in HCl and estimated, when it was found that the lead dissolved amounted to one grain in the 5oz. in Experiment XXIII., and to half a grain in the 5oz. of Experiment XXIV., the previous heating at 105° F. for 24 hours having doubled the power for action of the water on lead in Experiment XXIII.

The next three experiments are given as having a little special interest, and as being corroborative of the fact that the non-action of a distilled water is due to the presence of an alkaline "obstruction," which may be carbonate of ammonia.

Experiments XXV., XXVI., XXVII.—In Experiment XXV. the water was a distilled water with an alkaline reaction, whose power of acting on lead was previously unknown.

In Experiment XXVI. the water was the same as in Experiment XXV., but to it was added six drops of a rather strong solution of perchloride of mercury in spirit and water. The water was made acid by the perchloride.

The result of Experiment XXV. was a slight patchy action, the inside of the tubes of lead being particularly affected. It was evident the water contained "obstruction."

In Experiment XXVI. a considerable continuous action occurred, with production of solid lead-salt, closely simulating or identical with that of a distilled water that acted of its own accord.

Here we see perchloride of mercury, which, by the way, was added with quite a different object, setting up a great action in a water that otherwise would have acted very slightly. The explanation, no doubt, is that the obstruction was removed by the mercury persalt. We saw that the water was made acid by it, so that there was an excess of the perchloride, which latter has naturally an acid reaction.

Experiment XXVII.—The same water as in the last two experiments was boiled in a glass flask one minute. Its alkalinity was by this means increased. Lead was then put into it, but after 24 hours no solid oxyhydrate had been produced. Ten drops of the solution of $HgCl_2$ were added, but the reaction of the water remained just alkaline, and there was but an insignificant patchy action on the lead after many hours.

This last experiment, however, is scarcely comparable with Experiment XXVI., because the lead was put in the water 24 hours before the perchloride, and had consequently become coated with carbonate of lead, a fact which it was not in the power of the perchloride to undo, especially as not enough had been added to the water to give it an acid reaction. Possibly if more perchloride had been added the coat of insoluble salt, with which the lead was covered, might have been dissolved off. The next experiment proves that the coat or film by which the lead is protected in the case of a hard water can be dissolved off by a small amount of nitric acid in a distilled water, and the usual action with production of oxyhydrate will follow.

Experiment XXVIII.—Pieces of clean lead were placed in a dish and partly covered with a rather hard tap water (New River). The lead was occasionally turned about in the water, and thus being exposed alternately to water and air was soon covered with a thin dark film which showed a coppery iridescence after being allowed to dry in the air. A distilled water, which acted strongly on lead, being placed in a jar as before, this lead was dropped into it.

After 24 hours the lead was unaffected. There was no production of oxyhydrate, and no lead in solution.

Nitric acid was now carefully added until just appreciable to litmus paper.

After 48 hours there was no apparent action, but the water contained much lead in solution. Water still faintly acid.

After 72 hours the water was alkaline, and the production of solid white lead-salt had begun, the lead and the bottom of the vessel being partly covered with it.

After 144 hours the action was proceeding, and the crystals of solid lead-salt were much increased. There was considerable scum on the surface of the water.

Before proceeding to study further the effect of adding certain acids and salts to a distilled water that already acts on lead with production of crystalline oxyhydrate, with intent to discover any modification in the action that may be caused by such addition of acids and salts, it will be profitable to make a preliminary examination of the oxyhydrate itself. The production of a crystalline oxyhydrate of lead by action of water on lead has a long time been recognized, as reference to the text books will show. The relative proportions of hydrate to oxide may perhaps vary according to circumstances, and the formula PbO, Pb2HO may not always represent the compound formed. This, however, is not very material. It is enough to know that the action results in the formation of oxide of lead, a portion of which is combined with the element of water in the form of hydrate. It is convenient for our present purpose to speak of the compound as oxyhydrate simply, but when an alkaline base, such as this oxyhydrate of lead, is placed in a solution containing other salts, there is always a transference of a certain portion of the acid radicles present to the base, whatever were the bases with which they were previously combined. In the experiments already set down, it is quite apparent that other salts of lead, besides simple oxyhydrate, are produced even in distilled water by combination of a portion of the acid radicles present in the ammonia salts with the basic lead-salt as it is formed. Carbonic acid gas, whether existing as carbonate of ammonia or as free carbonic acid, will be always appropriated in like manner with production of basic carbonate of lead.

The oxyhydrate, removed by a pipette from the jar in which it has been produced by the action of distilled water on lead, is seen to be composed of very small colourless crystals, which show a tendency to cling together and form masses. These crystals are only slightly soluble in distilled water, the solubility varying, according to the author's experience, from $\frac{1}{200}$ to $\frac{1}{30}$ of a grain per gallon in different distilled waters. That is to say, that when distilled water which has been some time in contact with the oxyhydrate is run through filter paper, the filtrate does not contain more than this quantity of lead. But if the supernatant and apparently clear water be removed from one of the jars in which the oxyhydrate is being formed, rendered acid and tested with H_2 S, generally more lead will be found in it, due to the small crystals that were held in suspension. When the crystals are shaken with distilled water not more than the quantity mentioned actually enters into solution, but the reprecipitation of the whole of the lead-salt takes place rather tardily, the suspended crystals giving a glistening appearance to the water for some time. When the oxyhydrate is boiled with distilled water, not a greater, but a decidedly smaller quantity is afterwards found in solution. A water which will dissolve $\frac{1}{30}$ grain per gallon in the cold may not contain more than $\frac{1}{500}$ grain per gallon when boiled and allowed to cool before filtration. This difference must be due to the existence of a basic salt of lead, perhaps basic nitrite, which is more soluble in cold water than the main portion of the oxyhydrate, and which is either decomposed or altered upon boiling along with an excess of oxyhydrate. The crystals are dissolved with slight effervescence on addition of excess of hydrochloric nitric or acetic acids. With sulphuric acid, sulphate of lead is formed. The gas evolved has generally a nitrous odour, but this cannot always be detected on account of the very small quantity given off. The compound always gives a blue reaction with starch, iodide of potassium, and acid; more clearly got with sulphuric than acetic acid owing to the formation of yellow iodide of lead with the latter acid. When thrown upon a filter and repeatedly washed with distilled water it at length ceases to give the blue reaction, but gives more effervescence, due to absorbed CO_2. The idea expressed above, that a basic nitrite forms a portion of the compound, and that this is the portion which is slightly soluble, here finds corroboration. It may be nitrite or hyponitrite, according to circumstances, or, rather, be a basic compound of lead containing either NO or NO_2—after exposure to air always the latter. The oxyhydrate is freely soluble in pure caustic soda solution and in common lime-water; less so in ordinary solution of ammonia or in liquor potassæ. Ammonia-salts being present in the water, its solubility is increased, and nitrate of ammonia is more potent to dissolve it than chloride. When shaken with solution of chloride of ammonia, the odour of free ammonia is detected in the mixture. Shaken with solution of sulphate of magnesia, the appearance of the precipitate becomes slightly altered, probably due to formation of a little sulphate of lead. In solution of ferrous sulphate it causes a yellow precipitate of oxide of iron, which increases much on the mixture being allowed to stand an hour or two. With solution of ferric chloride a large yellow precipitate is immediately obtained, and in both cases much lead is dissolved. When carbonic acid gas is passed into water containing the crystals, and the water is immediately run through a filter paper, much dissolved lead is found in the filtrate.

In the following table the amount of lead which entered into solution when the oxyhydrate obtained from a distilled water action was placed in solution of various salts is set forth. One ounce of the solution of each salt, or salts, was put into an ounce-and-a-half phial and an indefinite but excessive quantity of the oxyhydrate was added. The mixtures having been allowed to stand, with occasional and equal agitation, for 36 hours, were filtered through paper and the lead estimated in the filtrate.

Table showing rate of solution of lead-oxyhydrate in distilled water containing various salts dissolved in it, and in certain other waters, the lead-salt being exposed to the action of the waters for 36 hours.

No.	Description of Water.	Lead found in the Filtered Solution.
1	Distilled water alone, cold	$\frac{1}{150}$ grains per gallon
	Distilled water containing—	
2	1 part in 1,000,000 nitrate of ammonia	$\frac{1}{15}$,, ,,
3	1 grain in gallon carbonate of ammonia	$\frac{1}{15}$,, ,,
4	1 ,, ,, chloride of ammonia	$\frac{1}{10}$,, ,,
5	3 ,, ,, ,, ,,	$\frac{1}{3}$,, ,,
6	1 ,, ,, chloride of sodium	15 ,, ,,
7	3 ,, ,, ,, ,,	$\frac{1}{7}$,, ,,
8	2 ,, ,, bicarbonate of sodium	$\frac{1}{5}$,, ,,
9	2 ,, ,, nitrate of potassium	$\frac{1}{15}$,, ,,
10	2 ,, ,, sulphate of magnesium	$\frac{1}{10}$,, ,,
11	2 ,, ,, sulphate of iron	$\frac{3}{4}$,, ,,
12*	0·8 ,, ,, sulphate of calcium 0·6 ,, ,, sulphate of magnesium 0·8 ,, ,, chloride of sodium 0·2 ,, ,, nitrate of potassium	$\frac{1}{15}$,, ,,
13	New River water alone	$\frac{1}{7}$,, ,,
14	Huddersfield water as supplied to Mirfield, Yorks	$\frac{3}{4}$,, ,,
	Huddersfield water as supplied to Mirfield, Yorks, after ten days	$\frac{1}{6}$,, ,,
15	Boiling distilled water	$\frac{1}{500}$,, ,, or a small trace.

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* In imitation of solids found in a soft water collected from a brook at Holmfirth, by Wanklyn ("Wanklyn's Water Analysis," pp. 146).

On shaking the oxyhydrate with the water which contained carbonate, *i.e.*, Nos. 3, 8, and 13, the appearance of the undissolved remnant of lead-salt was altered. The crystals became more silky or micaceous in appearance when shaken up in the water. Precisely the same thing occurred with Mirfield water.

By the foregoing we learn that most of the salts which commonly occur in natural waters possess considerable power of causing a portion of the oxyhydrate of lead to enter into solution. This we may suppose to be due to the formation of various salts of lead, double decompositions taking place between the hydrate of lead and the ammonia-salts, calcium-salts, etc., that are present. The compounds of lead thus formed at the expense of a portion of the acid radicles of the other salts present, sulphates, nitrates, etc., being more soluble than oxyhydrate of lead itself. The degree of basicity of the salts of lead formed depends upon the relative quantities of lead oxyhydrate and other salts present, and also upon the length of time allowed for them to act upon each other. As the probability is that the more basic the compound the less soluble it will be, it may happen that where a water is acting on lead with continuous production of oxyhydrate, more lead will be found actually dissolved during the first few hours of the action than later on. It was found, for instance, that Mirfield water left in contact with excess of oxyhydrate for more than a week did not contain dissolved more than a quarter as much as it did after 36 hours only. The explanation is that the acid in Mirfield water dissolved the oxyhydrate, first forming a neutral salt, or a salt of low basicity, freely soluble in water; but this salt being left in contact with the excess of oxyhydrate, the ultimate result was a salt of much higher basicity much less soluble in water. In experiments which follow, we shall obtain frequent exemplification of the same thing, and prove that a continuous oxidation of the lead, going on in waters that were at first acid, leads to a deposition of the lead that was at first dissolved, and from containing much lead in solution such water may, within a few hours, come to contain very little lead in solution. The basic compounds of lead which are likewise produced by appropriation of a portion of the acid radicles previously combined with other bases in a water, when such water acts on lead with continuous production of oxyhydrate, will vary in basicity and in solubility, probably arriving at last at an ultimate basicity and a constant solubility. Strict regard must be had to this liability to change in solubility of the lead-salts produced in any experiment to determine the power of a water to take up lead. Up to a certain point there will always be an increase in the quantity of lead dissolved, and beyond that a diminution. The fractions of a grain per gallon discovered in solution in the various waters of the preceding table may not represent the highest amounts that those waters can in any time dissolve. They represent only the amounts which were in solution at the end of 36 hours respectively.

Experiments XXIX., XXX., XXXI., XXXII., XXXIII., XXXIV.—In these experiments a distilled water which acted on lead with production of oxyhydrate was used, a portion of the same water being used in each case. The original reaction of the water was as nearly neutral to litmus and cochineal as possible. Five ounces of water in a glass jar were used as before, the cleaned lead being put in after the addition to the water of the various acids as below.

Experiment XXIX. was made with the distilled water alone.

Experiment XXX.—The distilled water, with sulphuric acid added in the proportion of 1 grain H_2SO_4 per gallon.

Experiment XXXI.—The distilled water, with 1 grain HNO_3 per gallon.

Experiment XXXII.—The distilled water, with 10 grains HNO_3 per gallon.

Experiment XXXIII.—The distilled water, with 1 grain HCl per gallon.

Table showing the action of a distilled water on lead, and the action of the same water when rendered slightly acid by addition of Sulphuric, Nitric, Hydrochloric, and Acetic Acids respectively.

No.	Water used.	Action apparent to the Eye.	Lead found dissolved in the filtered water.	Total lead occurring as lead-salt in the 5oz. of water used.	Length of experiment.
29	Distilled water alone.	There was much apparent action, the production of crystalline oxyhydrate being continued from first to last.	$\frac{1}{100}$ grain per gallon.	1 grain (= 32 grs, per gal.).	84 hours.
30	Distilled water with 1 gr. per gal. H_2SO_4 added.	After 12 hours a considerable amount of solid white lead-salt produced and deposited on bottom of vessel and on lead; this was afterwards little, if at all, increased.	$\frac{1}{8}$ grain ,, ,,	$\frac{1}{8}$ grain (= 4 grs. per gal.).	84 hours.
31	Distilled water with 1 gr. per gal. HNO_3 added.	Solid lead compound produced apparently greater in amount than in last experiment. There was more scum on the surface of the water.	$\frac{1}{3}$ grain ,, ,,	$\frac{3}{8}$ grain (= 12 grs. per gal.).	84 hours.
32	Distilled water with 10 grs. per gal. HNO_3 added.	Apparent action slight. At end of experiment there was a trifling deposit of solid lead compound which occurred during the last few hours of the experiment.	11 grains ,, ,,	Not measured, but much less than others.	84 hours.
33	Distilled water with 1 gr. per gal. HCl. added.	Apparent action about the same as in water which contained H_2SO_4, the deposit of lead compound taking place during first 12 hours.	$2\frac{3}{4}$ grains ,, ,,	$\frac{1}{8}$ grain (= 4 grs. per gal.).	84 hours.
34	Distilled water with 1 gr. per gal. $HC_2H_3O_2$ added.	A considerable deposit of solid lead compound occurred, but did not appear to be increased after the first 12 hours.	$3\frac{1}{2}$ grains ,, ,,	$\frac{3}{16}$ grain (= 6 grs. per gal.).	84 hours.

Experiment XXXIV.—The distilled water, with 1 grain $HC_2H_3O_2$ per gallon.

After addition of the acid the water had, in each case, a decided acidity. In each case the amount of lead in solution was estimated by filtering a portion of the water. The amount of solid lead-salt produced was also estimated colorimetrically with H_2S, the lead being first removed from the water and the undissolved precipitate dissolved with a few drops of HCl. In each case the solid lead-salt was readily dissolved by weak HCl. The result is given in the table on preceding page.

At the end of the 84 hours the waters which had been made acid to begin with were all decidedly alkaline in reaction, the acid in every jar having been more than neutralized by the oxyhydrate produced. The lead when removed from either jar, and allowed to dry in the air, was seen to be covered with a white bloom or fur. What had happened was this:—The water had power in the first instance to produce oxyhydrate. This was dissolved as fast as produced by the acid in the water, until the acid was more than neutralized. The salt of lead, which as a neutral or slightly basic salt was dissolved in the water, was precipitated on becoming more basic, and formed the deposit on the bottom of the jar of solid lead compound, and the bloom upon the lead. In covering the lead it stopped or retarded further action, for the supernatant water was a saturated solution of the same salt as that which covered the lead, and could never take up more, and so free the surface of the lead to the action of the water. In the case of the distilled water alone, the surface of the lead is not clogged in this way, because the product, which is in the condition of crystals of considerable size, has the natural propensity of falling off the surface of the lead as it is produced, and thus leaves the lead clean for further action. In the case of the water which contained so much as 10 grains HNO_3 per gallon, we should have had further deposit had more time been allowed. It appears that with equal amounts of acids, acetic acid and hydrochloric acid lead to more lead being retained in solution than nitric acid and sulphuric acid. This may be owing to the compounds of final basicity being more soluble in the case of acetic and hydrochloric than in the case of nitric and sulphuric acids. In 84 hours we see the total amount of lead-salt produced is far greatest in the distilled water to which no acid has been added. The next largest amount is in the water which contained nitric acid. We know that when only a trace of nitric acid is present the production of solid oxyhydrate of lead is not stopped (see Experiment XXVIII.), but after the acid has become neutralized it proceeds in the usual manner. When more nitric acid is present, the lead appears to be at first coated with a thick layer of basic nitrite, of very limited solubility, and which does not so readily fall off the surface of the metal. This retards, but does not prevent further oxidation. In the course of time the lead must be oxidized, oxygen being borne into the lead by repeated oxidation and reduction of the nitrite, and as time goes on the white lead-salt at the bottom of the vessel will be increased in quantity, being partly derived from a portion which falls off the surface of the lead, and partly from a further portion precipitated from solution.

The effect of the continued oxidation, at the surface of the lead, upon the lead at first taken up by a water to which nitric acid has been added, is seen in the next experiment, where it will be noticed that up to a certain point the solution becomes stronger in lead dissolved, and afterward when the water has become alkaline, and solid lead-salt is being produced at the bottom of the vessel, the solution becomes weaker, the basicity of the lead-salt in solution having become greater and its solubility less.

Experiment XXXV.—A distilled water of faintly alkaline reaction was made acid by adding to it nitric acid in the proportion of one grain HNO_3 per gallon.

After one hour the water remained clear and acid. A portion removed with a pipette and filtered, contained $\frac{1}{5}$ grain per gallon of lead.

After six hours the water was still clear, and no deposit on the bottom of the jar had occurred. The filtered water contained $\frac{7}{8}$ grain of lead per gallon.

After 18 hours the water was quite alkaline, and probably had been so for some few hours. Deposition of solid lead-salt was just commencing, the water having a very slight cloudiness.

After 24 hours the now alkaline water had a decided opalescence, and a very little deposit was seen at the bottom of the jar. A portion of the water removed, and run through filter paper, was found to contain $1\frac{1}{8}$ grain per gallon of lead. The water after being thus filtered was not perfectly clear.

After 48 hours the bottom of the jar was everywhere covered with a layer of white lead compound, some of which was also adhering to the sides of the jar and to the lead. The water had not yet cleared itself, but had a slight degree of cloudiness, and when a portion was removed with a pipette and placed in a dry test tube, it showed when shaken round and held up to the light a quantity of very fine crystals of lead compound held in suspension. These would be overlooked, unless the water were examined critically. The water passed once through filter paper was not totally cleared of these fine crystals. The filtered water contained $\frac{7}{8}$ grain per gallon of lead.

After 96 hours the water was clearer. A portion filtered was found to contain a quarter grain per gallon of lead.

After 144 hours it contained a quarter grain per gallon of lead.

Table showing the amount of lead found dissolved in a water made acid by addition of one grain per gallon HNO_3, after the lead had been exposed to the action of the water for increasing periods of time.

Length of time exposed.	Lead found dissolved in the water after filtration through paper.
1 hour.	$\frac{1}{5}$ grain per gallon.
6 ,,	$\frac{7}{8}$,, ,,
24 ,,	$1\frac{1}{8}$,, ,,
48 ,,	$\frac{7}{8}$,, ,,
96 ,,	$\frac{1}{4}$,, ,,
144 ,,	$\frac{1}{4}$,, ,,

There is another acid which has power of dissolving lead oxide, and which often gives an acidity to waters that otherwise would be neutral or even alkaline to a faint degree, and which, therefore, must not escape consideration. This is carbonic acid.

The effect of carbonic acid in a water that has power of acting on lead to produce oxyhydrate is very analogous to that of any other acid. The first portion of oxyhydrate produced is dissolved by it, and a considerable fraction of a grain per gallon of lead may exist in solution as acid carbonate. Soon, however, the production of oxyhydrate continuing, the carbonic acid is neutralized and more than neutralized, and a basic carbonate of lead is formed which is insoluble, and thus the lead which was at first dissolved is withdrawn from solution. The utmost amount of carbonic acid gas that water can hold in solution at common atmospheric pressure is about its own volume, and a litre of CO_2 weighs about two grammes. But in a general way the strength of the solution of CO_2 in natural waters approaches nowhere near the saturation point. Rain-water is said to contain one cubic inch of CO_2 per gallon, and, according to Miller, Thames water at Kingston contains 30·c.c. per litre. We must also bear in mind that an extra molecule of the acid will always be required to form the soluble acid carbonate, and remembering these things it becomes patent that no very large quantity of lead is likely to be found dissolved in any ordinary natural water by reason of the carbonic acid that it may contain. The basic carbonate ultimately produced in such a water, not being great in amount, attaches itself chiefly or wholly to the surface of the lead, little or none being found at the bottom of the vessel. The bloom-like covering which in this way is formed upon the lead protects the lead from further action of the water, or at least greatly retards the action. It closely resembles the bloom or fur which covers the lead exposed to water containing any other acid, and is very dissimilar to the thin, closely-fitting iridescent film that covers the lead exposed to water containing any alkaline carbonate.

Experiment XXXVI.—A distilled water, that acted on lead with production of oxyhydrate, had washed carbonic acid gas passed through it for some minutes at common atmospheric pressure. The water, which now had a decided acidity to litmus, was placed in a jar with lead as before. From time to time, as below, water was removed from the jar with a pipette and run through filter paper, the lead in solution being estimated in the filtrate. The only apparent effect was a darkening of the lead, there being no production of white lead salt. At the end of the experiment, when the lead was removed and allowed to dry in the air, it was seen to be covered everywhere, excepting where it had been in contact with the glass, with white bloom, which it was not difficult to remove with a duster.

Table showing amount of lead dissolved by a distilled water which contained carbonic acid, after being in contact with the lead for increasing lengths of time.

Time Exposed.	Lead in Solution.
3 hours	$\frac{1}{15}$ grain per gallon
10 ,,	$\frac{1}{5}$,, ,,
30 ,,	$\frac{1}{100}$,, ,,
48 ,,	$\frac{1}{100}$,, ,,
96 ,,	$\frac{1}{100}$,, ,,

Having now studied the effect of adding free acids to a distilled water that acts on lead, attention may be turned to the effect of adding various salts to such a water previous to placing the water and lead in contact with each other. In experimenting with oxyhydrate produced by action of a distilled water, we have already ascertained the fact that the power of distilled water to dissolve it is greatly augmented by the presence of various salts in solution, so that we are prepared to find that the addition of such salts to an active water causes more lead to enter into solution when the water is brought into contact with metallic lead. Indeed, we have already found it to be the case when nitrate of ammonia is contained in the water as in Experiment XV., &c. Likewise we have proved that the addition of an alkaline carbonate to an active water causes the lead to be rapidly covered with a protective film which prevents further action of the water upon the lead. To find some salt or substance, in itself innocuous, that being placed in water shall give it the power of covering lead with a protective coat totally insoluble in acid or alkaline water, is up to this time an unsuccessful quest.

Experiments XXXVII to XLIV.—In these experiments the action of a distilled water alone was compared with the action of the same water when made to contain the various salts as indicated below. The exposure of the lead to the action of the water was continued for 72 hours with one exception. The object of the experiments was to discover whether the respective salts added to the waters would increase or deter the action, both in regard to the production of solid lead-salt, and its solution in the water.

Experiment XXXVII. was distilled water alone with lead as before.

Experiment XXXVIII.—The same water, but made to contain sulphate of calcium in the proportion of five grains per gallon.

Experiment XXXIX.—The same water, with chloride of sodium in the proportion of five grains per gallon.

Experiment XL. The same water, with phosphate of sodium in proportion of five grains per gallon.

Experiment XLI.—The same water, with phosphate of calcium in proportion of two grains per gallon, and hydrochloric acid in the proportion of one grain per gallon.

Experiment XLII.—The same water, made to contain a fused mixture sold as "silicate of soda," and which contained silicate and excess of alkali. The proportion added being one grain per gallon.

Experiment XLIII.—The same water, containing the same amount of silicate as in the last experiment, but the water finally made acid by addition of three drops of dilute hydrochloric acid to the five ounces of water.

Experiment XLIV.—The same water, made to contain an indefinite but large amount of the alkaline silicate, the solution being then rendered decidedly acid with HCl.

The result of these experiments is given in a tabulated form upon the next page. One thing demands attention particularly, and that is the development of the odour of chlorine in the waters which contained hydrochloric acid and chloride of sodium. It was by far most marked in those which contained the free acid, but was also very appreciable at the surface of the lead, in the waters to which chloride of sodium had been added. When sulphuric acid was dropped on to the surface of the lead removed from these particular waters, the odour of chlorine was most marked. The nitrous gas may also have been present, but if so its odour was lost in that of chlorine. The reaction obtained with iodide of potassium, starch and sulphuric acid was copious in these waters, and was no doubt due as much to chlorine as to nitrite. It would thus appear that when a water acts on lead in the presence of hydrochloric acid or chloride of sodium, the compound formed is not altogether a true basic chloride. The chlorine, or at least a part of it, enters into combination with a portion of the oxygen to produce an oxide of chlorine, which combines with the lead to form a hypochlorite. We cannot escape the inference that the presence of chlorides in a water, and particularly of

Table showing the modifications in the action on lead of a distilled water,
About 15 square inches of lead-surface exposed

No.	Water used.	Action apparent to Eye.	Appearance of lead when removed from water and dried.
37	Distilled water alone.	A continuous production of solid oxyhydrate from first to last.	... ...
38	Distilled water containing 5 grains per gallon $CaSO_4$. Reaction alkaline.	At end of the 72 hours the bottom of vessel covered with thin layer of white deposit.	Lead covered with a very thick layer of white fur.
39	Distilled water containing 5 grains per gallon $Na\,Cl$.	A continuous production of white lead-salt apparently identical with that produced from distilled water alone.	Smelt of chlorine, especially when $H_2\,So_4$ was dropped on to it.
40	Distilled water containing 5 grains per gallon Na_2HPO_4 crystals. Reaction alkaline.	At end of 72 hours the water was slightly opalescent, but there was no deposit worth mentioning.	Lead covered with a dark very iridescent film.
41	Distilled water containing 2 grains per gallon $Ca_3\,2PO_4$ 1 grain per gallon HCl. Reaction acid.	After 72 hours a considerable amount of white finely pulverulent deposit on bottom of jar.	Lead covered with white fur, slightly iridescent in places. It smelt of chlorine.
42	Distilled water containing 1 grain per gallon "silicate of soda." Reaction alkaline.	No apparent action.	Lead covered with thick white fur.
43	Distilled water containing 1 grain per gallon "silicate of soda," made decidedly acid with HCl.	At end of 72 hours there was a thin layer of deposit on the bottom of jar.	Lead appeared patchy, with white fur in some places and thin iridescent film in others. There was least of this film on the inner sides of the pieces of lead tube.
44	Distilled water containing much more "silicate of soda," and much more acid than in last experiment.	No apparent action.	... ...

caused by dissolving certain salts in the water previous to introduction of lead.
to action of five ounces of water.

Entire lead compound produced estimated as lead.	Lead actually dissolved.	Duration of Experiment.	REMARKS.
28 grains per gallon.	$\frac{1}{100}$ grain per gal.	72 hours.	The usual action of a distilled water.
4 ,, ,,	$\frac{1}{3}$,, ,,	72 hours.	Presence of Ca So_4 retards process of oxidation, but greatly increases the rate of solution of lead in the water.
36 ,, ,,	$\frac{1}{14}$,, ,,	72 hours.	Presence of Na Cl increases solid lead-salt produced; also causes more lead to enter into solution. Odour of Cl_2 suggestive of hypochlorite.
$\frac{1}{16}$,, ,,	... ...	72 hours.	The lead was in great measure protected by a film of phosphate, which covered it in alkaline water.
10 ,, ,,	$2\frac{3}{8}$,, ,,	72 hours.	The phosphate failed to protect the lead in the slightly acid water. Some time before end of experiment the water had become alkaline. The acidified water gave off odour of chlorine.
$\frac{1}{8}$,, ,,	... ...	72 hours.	Process of oxidation in great measure prevented, a result due probably more to carbonate than silicate of soda A considerable fraction of a grain of lead in solution.
$9\frac{3}{8}$,, ,,	... ...	72 hours.	The lead partly protected by patches of film of silicate. At end of examination the water was alkaline, had an odour of chlorine, and gave a slight reaction with starch and KI without addition of acid. On adding acid reaction much greater.
50 ,, ,,	50 ,, ,,	24 hours.	A large amount of silica in a decidedly acid solution does not protect the lead.

hydrogen-chloride, may assist in the oxidation of the lead in a manner not dissimilar to that in which the oxides of nitrogen assist it.

The production of oxyhydrate of lead by distilled water is affected to a considerable degree by differences of temperature. The following experiments roughly show this.

Experiments XLV, XLVI, XLVII.—These experiments were performed simultaneously, five ounces of water and two pieces of lead being employed as usual.

Experiment XLV. was at a common summer-day temperature, averaging about 64° F. Action was soon apparent, and after twenty-four hours the action had proceeded uninterruptedly with continuous production of oxyhydrate.

Experiment XLVI.—Another portion of the same water as in Experiment XLV., the jar being placed in a water bath, the temperature of which was maintained at 105° F. and lead added as before.

After two hours there appeared to have been fully twice as much oxyhydrate produced as in Experiment XLV. in the same time.

After twenty-four hours the apparent amount of solid lead compound produced was far greater than in Experiment XLV. in the same time.

Experiment XLVII.—Another portion of the same distilled water as in two former experiments, the jar being put into a water bath, the temperature of which was maintained at 212° F., and lead added as before.

After five hours very little apparent action, only a few curdy floccula having been produced, the lead-salt produced being evidently far less in amount than in the two former experiments in the same time. On account of the evaporation of the water the experiment had now to be stopped, as the water in the jar was no longer deep enough to cover the lead.

Experiment XLVIII.—A distilled water that acted on lead with production of oxyhydrate was placed in jar, the jar being then placed in the bath and surrounded with ice. The lead was then put into the water as before. The temperature of the water from the melting ice averaged 34° F.

After two hours a considerable amount of white lead-salt covered the bottom of the jar, and rendered the water opalescent.

After twenty-four hours the apparent action was great and continuing.

In Experiment XLVII., where the water in the jar was exposed to a temperature approaching that of boiling water, there was but little action. But we must remember the fact we have discovered in former experiments, that when a distilled water is raised to the boiling point in a glass vessel, its alkalinity is increased, an "obstruction" to the action being produced, which covers the lead with an insoluble coat and thus prevents further production of oxyhydrate. This is no doubt what happened in this case. Moreover, the heating of a water to 212° drives out the gases from the water, and so long as the temperature is maintained, any considerable absorption of oxygen from the air is impossible, and we have proved already that the necessary factor in the ultimate oxidation of the lead is O_2 absorbed from the air. Consequently, when the lead has removed all possible oxygen from the nitrate and nitrite in the water, the action must cease of necessity. Supposing a supply of oxygen remained at hand, even then in most instances the action would be stopped by the "obstruction" produced on boiling, which has the shape of carbonate presumably.

The experiment at the lowest temperature could not be compared with the other three experiments, because it was done with another distilled water at another time. From it we simply learn that a reduction of the temperature to near the freezing point by no means stops the oxidation of the lead. In future experiments we return again to this subject of effect of temperature.

We here bring to an end our study of the action of distilled water on lead, and will now proceed to the study of the action exhibited by some other waters. It will, however, be plain that in our previous experiments, having modified our distilled water by dissolving in it various salts and acids, we have in chief measure given it the properties of various other waters, and consequently in studying the action of distilled water on lead we have studied the action of most waters on lead.

The cause of action discovered in the case of distilled water, in the shape of the nitrogen oxides, may be expected to be present in any natural water, for it is impossible to suppose that this cause of action can for any considerable time be absent in such a water, though sometimes, as in the case of distilled water, the nitrogen oxide present may be so little in amount as to be difficult of detection, and yet be sufficient for the purpose under consideration. In most natural waters, however, a small or larger quantity of nitrate can be easily found, and when such waters are placed in contact with lead this metal will unfailingly reduce the nitrate, whether its quantity be small or large, unless the surface of the lead be covered with an insoluble coat and so be protected from the nitrate in solution. We have further studied in distilled water the dissolving effect exerted upon the oxide of lead, produced as above, by various acids and salts, and we may anticipate precisely the same results from these same acids and salts when they occur in a natural water. And lastly, we have studied in distilled water the effect of certain salts in preventing or retarding the oxidizing action by causing the lead to be covered with a totally or slightly soluble coat, fur, or film. To such salts collectively we have applied the term "obstruction," and have noted that carbonates form the chief and most perfect "obstruction." Thus we now find ourselves equipped with knowledge that will make the action of all other waters on lead easily intelligible.

II.—A WATER OBTAINED BY MELTING COMMERCIAL ICE.

The ice was obtained from a neighbouring fishmonger, to whom it was supplied by Gatti. It is said to be a natural ice from Wenham Lake. The water obtained by melting it had a hardness only equal to that of distilled water, 1 cc. of standard soap solution giving a large and permanent lather. Sulphates and chlorides could be detected in the unevaporated water. Nitrate was also present, and a small trace of nitrite. The reaction of this water was as nearly as possible neutral to cochineal.

This water was found to act rapidly on lead with production of solid oxyhydrate, the action being in no way distinguishable from that of distilled water. After action had taken place a much more copious reaction for nitrite than previously was obtained from the water, and the "oxyhydrate" produced also gave this reaction.

Experiment XLIX.—Melting ice was placed in a jar with lead as before, the jar also being surrounded with ice. The temperature for a great part of the experiment was 32° F., but rose in latter part to 42° F.

In half-an-hour the action was well established, and in two hours the bottom of the vessel was covered with a thin layer of white deposit.

After 24 hours the lead was removed from the water, a portion of which being filtered yielded $\frac{1}{40}$ grain per gallon of lead dissolved, and the total amount of solid lead-salt produced was equivalent to $\frac{1}{6}$ grain in the five ounces of water.

Experiment L.—The ice-water at 65° F. with lead as before. Action began quickly and proceeded uninterruptedly, and at the end of 24 hours the lead was removed.

The water contained $\frac{1}{50}$ grain per gallon dissolved lead, and altogether one-quarter grain of lead as lead-salt in five ounces of water.

Experiment LI.—The ice-water as before, but the jar was placed in a water-bath, the water of which was maintained at 120° F. The experiment was performed simultaneously with Experiment L. Action began as soon as the lead was placed in the water in a more marked manner than any hitherto observed, a thick cloud of white compound appearing immediately, which in a few minutes had given the water a considerable degree of opalescence.

After 24 hours it was evident that more solid lead compound had been produced than in the previous two experiments during the same time. The filtered water yielded only $\frac{1}{200}$ of a grain of lead dissolved; but the entire lead compound produced in the five ounces of water was equivalent to $1\frac{1}{8}$ grain of lead.

Efforts were next made to ascertain the rate of action at 160° F. and 212° F., but owing to the evaporation of the water it was found impossible to keep the action going for any considerable time as in the last experiments. The information obtained tended, however, to show that the action is not so rapid at these higher temperatures as at 120° F. The reason of this, as already stated, is partly on account of a tendency to development of obstruction at high temperatures by decomposition of organic matter or solution of alkali or silica from the glass, and partly to the oxygen being driven out and kept out of the water so long as its temperature remains raised. The fact of a heated water being unable to dissolve so much of the oxyhydrate as a cold water may have its reason partly in the loss of free carbonic acid gas, but chiefly in decomposition by heat, or alteration of constitution of the oxynitrite which exists along with, and is more soluble than the simple oxyhydrate. It will be remembered that when the "oxyhydrate" was washed repeatedly with distilled water it lost the power of giving the blue colour with starch, iodide, and acid.

Experiment LII.—The ice-water, as before, placed in bath at 160° F., and lead put in. After three hours the amount of solid lead-salt produced appeared decidedly less than that produced in the last experiment in the same time.

After 10 hours the five ounces of water in the jar was found evaporated to dryness. The jar was removed from the water-bath, water to the original amount added, and having been made slightly acid with HCl, the pieces of lead were lightly washed in the water and removed, and all the lead compound adherent to sides and bottom of jar being dissolved, the five ounces of water contained ⅓ grain of lead.

Experiment LIII.—The ice water in jar as before, the jar being immersed in water-bath, the water of which was at 212° F., and lead added. In this instance 6½ ounces of ice water used instead of five ounces. After one hour a considerable amount of flocculent or curdy compound of lead had been produced, but far less than in Experiment LI. in the same time.

After three hours the water had evaporated to ⅓ its original bulk, and the lead was partly above the surface of the water. The lead was now removed. A portion of the remaining water filtered yielded the slightest trace of lead dissolved, perhaps $\frac{1}{500}$ of a grain per gallon. The lead compound adherent to sides and bottom of the jar and suspended in the remainder of the water was equivalent to ⅛ grain of lead, produced from 6½ ounces of water.

The results of the foregoing five experiments are tabulated on the next page, and it will be seen that the rate of production of lead-salt is increased with the temperature at least up to 120° F. At higher temperatures its production is prevented or retarded. The amount of lead actually dissolved is inversely as the temperature.

Table showing the rate of production of oxyhydrate of lead in a soft water obtained by melting commercial ice, and its rate of solution in the water at different temperatures.

No. of Expt.	Temperature.	Length of Experiment.	Total lead as lead-salt found in the 5oz. of water.	Total lead as lead-salt in grains per gallon.	Lead found actually dissolved in the water in grains per gallon.
49	32° F., rising to 42°.	24 hours.	$\frac{1}{6}$ grain.	$5\frac{1}{3}$ grains.	$\frac{1}{40}$ grain.
50	65° F.	24 ,,	$\frac{1}{4}$,,	8 ,,	$\frac{1}{60}$,
51	120° F.	24 ,,	$1\frac{1}{3}$,,	36 ,,	$\frac{1}{200}$,,
52	160° F.	3 ,,	Much smaller quantity than at preceding temperature.		
53	212° F.	3 ,,	$\frac{1}{9}$ grain.	$2\frac{2}{3}$ gr. (circ.	$\frac{1}{500}$ (circ.)
			6½ oz. of water used) Not fairly comparable with 49, 50, 51.		

III.—RAIN-WATER.

The rain-water was collected in vessels placed upon the ground in a London garden. That caught on one day varied considerably from that caught on another in regard to the quantity of "free ammonia" which it contained, and in regard to its reaction to cochineal. Thus on October 7th water collected soon after it had begun to rain was found to have an alkaline reaction to cochineal, but another portion collected on the same day after much rain had fallen was decidedly acid to the same reagent. Again, a rain-water which was alkaline on the day it was collected, after storage in a stoppered Winchester quart for three months, was found to be acid. Another rain-water faintly alkaline to cochineal on the day collected had acquired an acid reaction four-and-twenty hours later. All this is suggestive of the idea that the acid (nitric) of rain-water is derived by the nutrification of organic nitrogenous material, which presumably exists in the air along with any necessary nitrifying ferment. This subject is very worthy of further investigation. The alkalinity observed in rain-water is, perhaps, sometimes due to carbonate of ammonia which has existence in the air of towns being one of the products of combustion of coal, etc., but it may also be derived by the breaking down of organic matter containing nitrogen, carbonate of ammonia having intermediary occurrence in the production of nitric acid. Under some circumstances the acidity of rain-water is due to H_2SO_4 washed out of the air. It has been stated that a rain-water that was alkaline at the time of collection afterwards became acid. A precisely contrary effect may, however, be sometimes noticed. For instance, a rain-water that was in the first place faintly acid, on being exposed for some days in a shallow dish became distinctly alkaline, and lost its power of acting on lead. When an acid rain-water is boiled in a glass flask it becomes alkaline, and the "obstruction" thus developed, as in the case of distilled water, is capable of protecting lead from the action of the water.

The action of fresh rain-water upon lead appears to be identical with that of distilled water, solid crystalline oxyhydrate of lead being produced, provided that the rain-water be not so acid as to be capable for a long time of dissolving oxide of lead as it is formed, nor so alkaline, by reason of contained carbonate of ammonia, as to prevent the formation of oxide of lead by giving the surface of the lead a protective coat.

Experiment LIV.—Fresh rain-water was placed in glass jar with lead as in previous experiments. Reaction of the water slightly acid.

After 24 hours the water was opalescent, and there was some deposit of white lead compound on the bottom of the jar. The reaction was now alkaline.

After this the action continued through the several days that it was under observation, with increasing quantity of solid lead-salt, exactly as in the experiments described with distilled water.

When the jar was loosely covered with an envelope, the odour of ammonia could be detected in it after some hours.

More scum was produced upon this water than upon distilled water under similar circumstances, which was taken as an indication that more lead was actually dissolved.

Experiments LV. and LVI.—Experiment LV. was made with a distilled water; Experiment LVI. with a rain-water of acid reaction. Five ounces of water and two pieces of lead were used as in previous experiments, and the two experiments were started simultaneously.

During the first 72 hours the amount of solid lead-salt produced appeared much greater in the distilled water. There was much more lead actually dissolved in the rain-water, however.

After 14 days the amount and character of the white lead-salt produced was about equal in both jars. It formed a deep layer at the bottom of either jar.

Experiment LVII.—Rain-water, as in last, was boiled in a flask for 10 minutes. The reaction was changed from acid to alkaline. When cold it was placed in jar with lead, as before.

After 48 hours a trifling action was apparent. It consisted in the production of a white patch on the inner side of the lead-pipe that lay in the water with its axis horizontal. There was also a very little white deposit on the bottom of the vessel, under the lead, near where it rested on the glass. The lead being taken out and replaced by clean pieces, action was established in precisely the same manner as described under distilled water, the first part of the white lead-salt produced having a curdy appearance, probably due to its containing carbonate of lead.

Experiment LVIII.—The boiled rain-water, as in last, but with ⅛ grain nitrate of ammonia dissolved in the five ounces of water. The nitrate added overcame the obstruction, and action upon the lead took place.

After 48 hours the product was considerable, and consisted of fine separate scales, which gave the water a silky or micaceous appearance when shaken up—that is to say, it was of different appearance to the compound produced by plain distilled water. Exactly the same thing occurred in Experiment XVI., &c., in which nitrate of ammonia was added to distilled water under similar circumstances. The difference in appearance of the product appears to be due to the presence of the carbonic radicle, along with comparatively much nitrate. Or possibly it is due to the sole effect of the nitrate, the first portion of the product consisting of a basic nitrite of lead, which contains more NO_2 than ordinarily. Later on the product had a rather curdy appearance, and we have already seen that curdiness denotes the presence of the carbonic radicle.

Experiments LIX. and LX.—The rain-water of Experiment LIX. was that collected on the morning of October 7th, and was faintly alkaline in reaction. Placed in the jar, with lead as in previous experiments, in half-an-hour action with production of solid lead-salt was apparent, the water having become opalescent, and a small collection of the white compound having begun to collect on the bottom of the jar near the pieces of lead.

After 24 hours action was continuing, and when shaken up the product was seen to consist of the micaceous-looking crystals, which gave the water a silky appearance, as in last experiment.

After 48 hours the production of these silky crystals was superseded by the production of the more ordinary crystalline scales, which do not possess the micaceous appearance.

No doubt the water contained a considerable quantity of nitrate, but the excess of nitric radicle having been used up in the production of micaceous-looking basic salt, afterwards the production of oxyhydrate proceeded as usual.

The rain-water of Experiment LX. was collected in the afternoon of October 7th, and was decidedly acid to cochineal. It was placed in a jar with lead, as in previous experiments.

For the first three hours the water remained clear, and at the end of that time a portion was found to contain lead dissolved in the proportion of ¾ grain per gallon.

After 12 hours the water was opalescent, and the bottom of the jar was covered with a very thin layer of lead-salt. A portion of the water was found to contain dissolved lead in the proportion of 1¼ grain per gallon.

After 24 hours the deposit on the bottom of jar was greater in amount. The filtered water contained two grains per gallon of lead.

After 48 hours still more solid lead-salt on the bottom of the jar, but the water contained only ¼ grain per gallon of lead dissolved.

After 96 hours there remained ¼ grain per gallon of lead dissolved.

Table showing amount of lead found dissolved in a rain-water after it had been in contact with the lead for different periods of time, the natural reaction of the rain-water to cochineal being distinctly acid.

Time exposed.	Lead in Solution.
3 hours.	¾ grain per gallon.
12 ,,	1¼ ,, ,,
24 ,,	2 ,, ,,
48 ,,	¼ ,, ,,
96 ,,	¼ ,, ,,

Here we have corroboration of the fact that when a water, by virtue of its acidity, dissolves the oxide of lead as it is produced, in a certain time the solution reaches a maximum strength, and that afterwards, owing to the basicity of the dissolved lead-salt becoming greater with the further production of oxide, and its solubility being for that reason lessened, a portion of the lead is thrown out of solution. Other circumstances remaining the same, the time in which the maximum strength will be reached will depend upon the quantity of acid present.

In all experiments made with rain-water, after action on lead had taken place, whether the oxy-hydrate occurred in solid crystals or was dissolved by acid in the water, a reaction denoting the presence of nitrite in the water and at the surface of the lead could always be obtained. This reaction was generally more decided than that obtained in the case of distilled waters, showing that a relatively larger proportion of nitrate is contained in rain-water than in distilled water.

Experiments LXI. and LXII.—A rain-water that was of alkaline reaction, and which contained much "free ammonia," being a portion of rain that first fell after some days of fine weather, was found to have a slight and sluggish action on lead, with production of white lead-salt. To a portion of it was added a strongly-acting distilled water, in proportion of about one part distilled to 100 parts rain-water. The mixture was allowed to stand aside for a week. At the end of that time, in comparison with another portion of the original rain-water, it was found to contain much more nitrate and nitrite than either the original rain-water or distilled water.

Experiment LXI. was, with rain-water, treated for a week with distilled water as above.

Experiment LXII. was with the original rain-water. Lead being put into the respective jars, the experiments were done simultaneously and side by side.

From first to last the production of oxyhydrate was greatest in the jar that had been exposed to the leavening action of the strongly-acting distilled water.

From this and from an experiment previously recorded, it would appear that stale distilled waters are rich in the influence which causes the oxidation of nitrogenous organic matter in water. The process set up by this—presumably bacterial—influence is a primal cause of the action of water on lead, the immediate cause being the continual reduction of the nitrate and nitrite—or in order to embrace all possibilities let us say oxidized nitrogen. When once the degradation of the organic matter has gone so far that an oxide of nitrogen has been produced, it is conceivable that bacterial influence is no longer necessary to the action of that water on lead, as the low oxides of nitrogen combine spontaneously with the oxygen of the air to form the higher oxides. What we have gathered from our experiments with water to which nitrate has been added leads us, however, to believe that the quickest and least interrupted action on lead takes place in those waters in which the breaking down of nitrogenous organic matter is actually going on, rather than in those in which the nitrifying influence is outworn by all the nitrogen having been fully oxidized into nitrate. This, of course, irrespective of any " obstruction " which the water may at the same time contain. What has been said however in reference to nitrification, and the hinted production of free nitric acid in rain water by such a process, is not intended to be taken as anything more than a speculation, to settle which would require much time and skill. The experiments touching upon this subject are too few and too crude to have more than a suggestive value.

IV.—WATER AS SUPPLIED TO MIRFIELD, YORKS, BY THE HUDDERSFIELD CORPORATION.

This is one of the moorland surface waters, notorious for lead-dissolving powers. Samples were received through the favour of Dr. Sproulle, of Mirfield.

Sample 1 had been drawn from the house-tap first thing in the morning, after the water had stood all night in the lead service pipe. It contained $\frac{1}{5}$ grain per gallon of lead.

Sample 2 had been collected from the tap after the water had been first allowed to flow through in a full stream for some minutes. It contained a trace of lead—about $\frac{1}{200}$ grain per gallon.

Sample 3 was taken by the turncock from the main in the street, in which Dr. Sproulle's house is situated, but not on the same day that samples one and two were taken. It contained $\frac{1}{25}$ grain per gallon of lead.

The occurrence of lead in the water of the main may be explained by a back current having taken place from the lead service pipes to the main, which is presumably of coated iron. The water in any street main from which water of this sort is conveyed to higher levels through lead service pipes must of necessity become contaminated. The increase in specific gravity caused in the water contained in the service pipes, through solution of lead, would lead to interchanging currents between the main and the service pipes. This will happen, even though the pressure be full and constant, but in the case of an intermittent supply of water the whole bulk of the water in the lead pipes may fall or be sucked back into the main. The amount of lead likely to be found in the water of the main depends on the number of lead pipes connected with it, and the quantity of water that has lately been drawn, and so is likely to vary between wide limits. It is quite plain, therefore, that in places like Mirfield no single inhabitant could protect himself by using an iron service pipe, or one lined with glass, or otherwise, inasmuch as he is liable to imbibe lead derived from his neighbour's pipe, as well as that derived from his own.

The Mirfield water gave evidence of containing nitrate and a very little nitrite; the presence of chloride and sulphate was readily detected in the unevaporated water, which also had a decided acid reaction to litmus and to cochineal. The hardness of the water was equal to that of town rain-water, *i.e.*, between 4° and 5°. When one part of New River water (containing 13 grains $Ca\ CO_3$ per gallon) was mixed with 20 parts of Mirfield water, the acidity of the latter was more than neutralized, the mixture being decidedly alkaline to cochineal. When the Mirfield water was boiled in a glass flask its acidity was lost, the boiled water being slightly but distinctly alkaline. Mirfield water was found to dissolve copper as readily as lead when placed in contact with the metal. It also dissolves zinc and iron.

Experiment LXIII.—Five ounces of the Mirfield water (sample 2) in jar with lead as in previous experiments.

After 10 minutes, on moving the jar, a little cloud of white compound was seen inside the tube of lead that lay horizontal, but this was afterwards dissolved, and was only produced at first on a part of the lead that was protected in a measure from the main bulk of the water, the production of oxyhydrate of lead going on there faster at first than the acid of the neighbouring water could dissolve it.

After six hours no solid lead compound worth speaking of had been produced, but the water contained half grain per gallon of lead dissolved.

After 12 hours water still acid.

After 36 hours water still on acid side of neutrality; no solid lead compound produced.

After 60 hours the water had become alkaline. There was a white bloom on the lead, visible as it lay in the water.

After 84 hours the bottom of the vessel was stained with a trifling amount of white deposit. The water yielded 1½ grain per gallon of lead dissolved. The water gave a decided reaction with starch, iodide and acetic acid, much more than previous to its action on lead. The pieces of lead removed and dried in the air were seen to be covered with a thick layer of roughish white fur. Moistened with sulphuric acid it gave off a decided odour of nitrous gas, and a drop of solution of KI and starch being added, the dark blue coloration was obtained in a copious and marked manner. When a piece of the lead was washed in a little distilled water, this water gave the same reaction, denoting nitrite.

Experiment LXIV.—The Mirfield water, as in last, had carbonate of ammonia dissolved in it to the extent of two grains per gallon. Reaction of water now decidedly alkaline. The water now placed in jar with lead as before.

In a short time the lead appeared darkened, just as it appears when placed in a hard water, and it was evident the carbonate was protecting the lead.

After six hours, as no further action had taken place, the lead was removed, cleaned, and returned.

After two hours there had been a very little white deposit produced from the upright piece of lead, near which it lay on the bottom of the jar.

After two more hours, as no further action had taken place, the lead being again coated, the lead was again removed, cleaned, and returned.

After 12 hours it was evident the "obstruction" had been sufficiently removed, for action with production of solid lead-salt was well established.

After 60 hours action was continuing precisely as in distilled water with production of more and more crystalline oxyhydrate of lead.

After 120 hours the filtered water was found to contain $\frac{1}{100}$ grain per gallon of lead, whilst the solid oxyhydrate produced was equal to $\frac{5}{8}$ grain of lead in the five ounces of water.

Experiment LXV.—Mirfield water mixed with $\frac{1}{20}$ of its volume of New River water. The reaction of the mixture to cochineal was alkaline.

After three hours there was no apparent action, excepting that the lead was darkened. It was removed from the water and allowed to dry in the air, when it was seen to be covered with a thin iridescent film which evidently protected it. It was cleaned and returned to the water.

During the next 12 hours the lead was twice removed from the water, cleaned, and returned. After the third cleaning the "obstruction" was removed, and action with production of white lead-salt was well established. The first portion had a curdy appearance, but the usual scaly masses of crystals were formed later on.

After 72 hours the action was continuing rapidly, and much oxyhydrate had been produced; it was equal, in fact, to $\frac{3}{8}$ grain of lead in the five ounces of water, which also contained $\frac{1}{40}$ grain per gallon of lead actually dissolved.

Experiment LXVI.—Mirfield water (sample 3) was boiled in a glass flask for three minutes. Its reaction was then alkaline to cochineal. It was placed in a jar with lead as before.

After 24 hours the surface of the lead was dulled, but there was no other apparent action, but the water contained dissolved $\frac{1}{18}$ grain per gallon of lead.

After 48 hours the appearance was the same, and the amount of lead in solution the same.

After 96 hours there was no further action; the water still contained $\frac{1}{18}$ grain per gallon of lead. The water, to begin with, had contained $\frac{1}{25}$ grain per gallon. The lead being now removed from the water and allowed to dry, was seen to be covered with a very thin film, which, however, had protected the lead after a very small fraction of a grain per gallon had been added to that already in solution.

Experiment LXVII.—Mirfield water (sample 3), in jar, with lead, as before.

After 24 hours a portion of the water removed and filtered contained $\frac{1}{7}$ grain per gallon of lead.

After 48 hours water similarly treated contained $\frac{1}{6}$ grain per gallon.

After 96 hours it contained $\frac{1}{60}$ grain.

Tested at end of 48 hours the water was found to have become alkaline.

Experiment LXVIII.—Mirfield water (sample 3), as in last, but water being removed at different times with a pipette, the lead was estimated without filtration of the water.

After four hours it contained $\frac{1}{12}$ grain per gallon of lead; after 10 hours, $\frac{1}{6}$ grain; after 24 hours, $\frac{1}{4}$ grain; 48 hours, $\frac{2}{5}$ grain; 96 hours, $\frac{1}{30}$ grain.

Table showing the amounts of lead dissolved by Mirfield water in the several stages of its action upon the metal.

Water.	Time of Exposure.	Lead found in the Water.
(*a*) Mirfield water, which previously contained $\frac{1}{25}$ grain per gallon of lead. The portions of water removed filtered through paper before estimation of lead...	24 hours.	$\frac{1}{7}$ grain per gallon.
	48 ,,	$\frac{1}{6}$,, ,,
	96 ,,	$\frac{1}{60}$,, ,,
(*β*) Mirfield water as above. The portions of water removed with a pipette, not being filtered before estimation of lead.....................	4 ,,	$\frac{1}{12}$,, ,,
	10 ,,	$\frac{1}{6}$,, ,,
	24 ,,	$\frac{1}{4}$,, ,,
	48 ,,	$\frac{2}{5}$,, ,,
	96 ,,	$\frac{1}{30}$,, ,,

Experiment LXIX.—The Mirfield water of one of the above experiments, after lead had been exposed in it for 96 hours, had the lead removed from it and fresh clean lead put into the water in its place.

The result was the continuous production of solid crystalline oxyhydrate of lead, which, of course, was no longer dissolved, as the solvent power of the water had been exhausted in the previous action.

The degree of acidity of the different samples of Mirfield water obtained evidently varied. The water used in Experiment LXIII. had much greater power of dissolving lead, due to its greater acidity, than the water used in the experiments in the table above. This last water, however, contained $\frac{1}{25}$ of a grain per gallon of lead, and must, therefore, have been in contact with lead for a longer time than the other water, which only contained $\frac{1}{200}$ grain per gallon. Contact with lead results in loss of acidity.

In the case of Mirfield water which is in contact with lead, when the water becomes alkaline and the strength of the solution of lead begins to grow less, no precipitate, or comparatively little, occurs upon the bottom of the vessel, the lead-salt withdrawn from solution attaching itself to the surface of the lead to form the thick fur observed. Probably, had the water possessed a greater degree of acidity, more of the basic salt produced would have found its way to the bottom of the jar, as in the experiments with distilled water to which acid had been added. The acid in Mirfield water was, however, considerably less than the equivalent of 1 grain HNO_3 per gallon, which was the smallest quantity used in the experiments with distilled water. The insoluble fur which thus came to coat the lead prevented further action with production of oxyhydrate. It must not be forgotten, however, that this fur would be very rapidly dissolved off by a fresh supply of the acid water, and a great contamination of the water would occur in a much shorter time than if the lead were clean and the water had to produce the oxide before dissolving it. An experiment was made at 120° F. to ascertain the effect of greater heat upon the action of Mirfield water. As we have proved already that the production of oxyhydrate takes place much more rapidly at 120° F. than at lower temperatures, we might anticipate the result in the case of Mirfield water. The acid is neutralized at a quicker rate, the water contains its maximum amount of dissolved lead in far shorter time, and this dissolved lead is afterwards quickly withdrawn. In fact, at the end of three hours the action has gone through all its stages, and the same result is arrived at as after ninety-six hours at common temperature, the only difference being that even a smaller fraction of a grain per gallon of lead remains in solution in the heated water.

Thus we find that the action of Mirfield water upon lead is practically identical with distilled water which has been given an artificial acidity by mixing with it a small quantity of either of several acids, also with rain-water, which is naturally acid.

V.—WATER FROM OKEHAMPTON, DEVON, BEING A SAMPLE OF THE PUBLIC SUPPLY TO THAT TOWN.

A sample of this water was obtained by favour of Dr. Young, Medical Officer of Health to the Okehampton Urban and Rural Districts. Dr. Young has been kind enough to supply the author with some interesting information concerning this water, including an analysis and the result of some experiments, conducted by himself, upon the lead-dissolving powers of the water, which by his permission are given below.

In regard to its origin, the water is mainly derived from a spring in the granite, but consists also in part, of a varying proportion of surface water. It has generally an acid reaction, and the acid it contains gives it the power of taking up lead when brought into contact with that metal. Its degree of acidity appears to vary, which, indeed, is the case with all acid waters, and its composition no doubt will vary slightly from time to time. Dr. Young regards it as a soft water of excellent quality from a hygienic point of view, apart from its lead-dissolving property. The following is Dr. Young's analysis, and the result of his experiment upon the lead-dissolving power of the water.

Analysis of water of Okehampton water supply, derived from springs on Dartmoor, and from the moorland surface.

Total solids. In grains per gallon.	Chlorine. In grains per gallon.	Sulphate. In grains per gallon SO_4	Nitrate. In grains per gallon.	Nitrite. In grains per gallon.	Free Ammonia. In parts per million.	Albuminoid Ammonia. In parts per million.
5·0	1·2	1·2	·1	·0	·01	·06

The microscope showed very little suspended vegetable or mineral matter, although the water is not filtered.

In experimenting on the lead-dissolving power, Dr. Young allowed the water to stand in the pipe (an old one) by which his house was supplied, for different periods of time, the lead being estimated in the water after each period of exposure.

Dr. Young's experiments upon the lead-dissolving power of Okehampton water. (Compare with Experiment LXVIII., Mirfield water.)

Length of time water was allowed to stand in pipe.	Lead found in the water in grains per gallon.
5 hours.	·3
6 ,,	·35
17 ,,	·5
24 ,,	·8
48 ,,	1·0

In these experiments the water was on at full pressure from the main, but on screwing down a tap situated in the service pipe outside the house, the water in the pipe was relieved of the pressure from the main; but when other experiments were performed with this modification the amount of lead entering into solution during a given time remained much as before, which appeared to prove that pressure of water exercised very little influence upon the rate of solution of lead. Dr. Young also experimented with a new lead pipe, but the amount of lead taken up from it did not materially differ from that taken up from the old pipe.

The supply of Okehampton water received was found to be acid to litmus, but faintly alkaline to cochineal. In this it differed essentially from Mirfield water, which, it will be remembered, was decidedly acid to cochineal. The acidity as thus exhibited by Okehampton water would therefore appear to be due merely to a little free carbonic acid. The acidity, however, which caused the water to take up lead in the quantities as exhibited in the table above, would have been due to the presence of some other acid than carbonic. If any such had previously existed in the particular sample of water received it must have been, in some way, neutralized. The water contained a mere trace of lead and a much larger trace of iron, perhaps $\frac{1}{300}$ grain per gallon of lead and $\frac{1}{50}$ grain per gallon of iron.

Experiments performed with this water with pieces of lead pipe in a glass jar yielded no very positive results, the further amount of lead taken into solution by it being only small and insignificant in comparison with the quantity taken up by some other waters which have already been brought under notice. It has been stated that apart from a weak acidity appreciable to litmus, due no doubt to a small quantity of carbonic acid, the single sample of Okehampton water obtained was faintly alkaline in reaction. This alkalinity may have been accidentally derived from the bottle in which it was sent or otherwise. Dr. Young informs the author that the water is more generally faintly acid to cochineal, and has considerable power of dissolving lead, as indeed his experiments witness. In that case Okehampton water must closely resemble Mirfield water, the results of an examination of which are given under the last heading.

Experiment LXX.—The Okehampton water as described above was placed in a jar with two pieces of lead, as in previous experiments.

Water was removed with a pipette, and tested for lead without filtration, after the following periods of exposure:—Six hours, 24 hours, 48 hours, 96 hours.

At the end of six hours the water was alkaline to litmus.

The amount of lead found in the water at the end of the periods of time specified became increasingly greater, at least for some considerable number of hours, but at the most the fraction of a grain per gallon of lead found was but very small. The approximate differences observed in the amount of lead present after increasing periods of exposure, are given in a table below.

At the end of the experiment the water was tested for nitrite, which was found readily, and showed that some amount of oxidation of lead had taken place, a portion of the nitrate present having been reduced.

On removing the lead from the water and allowing it to dry, it was seen to be covered with soft white fur, and not with hard iridescent film. This fur must have owed its production partly to the small amount of carbonic acid originally present in the water, and partly to the sulphate which was also present. The increasing quantity of lead which entered into solution may have been due to the increasing formation of sulphate of lead, the sulphuric radicle originally present in the water being for some time slowly and continuously utilized for this purpose.

Table showing the action upon lead of a sample of Okehampton water that had an alkaline reaction to cochineal after different periods of exposure.

Length of time exposed.	Lead found in solution.
6 hours.	$\frac{1}{200}$ grain per gallon.
24 ,,	$\frac{1}{100}$,, ,,
48 ,,	$\frac{1}{60}$,, ,,
96 ,,	$\frac{1}{60}$,, ,,

Experiment LXXI.—Okehampton water as in last experiment, placed in jar with lead as before.

After 24 hours, as there was no production of solid lead-salt, excepting the little at the surface of the lead, and only a very small fraction of a grain per gallon of lead in solution, the lead was removed and substituted by fresh clean pieces. A trifling action ensued, with production of solid white lead compound. After a few more hours the lead was again removed, and other pieces of clean lead put in its place. A decided action with production of oxyhydrate of lead was then set up, and went on continuously as in the case of distilled water, so that after 72 hours a deep layer of the crystalline lead-salt had collected at the bottom of the jar.

The supernatant water gave much ampler evidence of containing nitrite than that of the last experiment.

VI.—THE WATER OF THE NEW RIVER COMPANY, AS SUPPLIED TO A LARGE PART OF THE NORTHERN AND CENTRAL DISTRICTS OF LONDON.

This water contains about 20 grains total solids per gallon, including 13 grains of carbonate of calcium, and over one grain of nitrate, as well as chloride sulphate, etc.

Experiment LXXII.—New River water from house tap was placed in jar with lead as before.

After 48 hours there was no production of solid oxyhydrate, and the water contained a bare trace of lead in solution. The lead when removed and dried was covered with a dark thin and close-fitting iridescent film, which was no doubt due to the formation upon the lead of an insoluble basic carbonate. This protected the lead from the further action of the water.

Experiment LXXIII.—New River water with two grains of nitrate of potassium dissolved in the five ounces, and lead as before.

After 24 hours the lead was protected as before, but there was a very little white deposit on one piece of lead near where it touched the glass. This was evidently formed before the carbonate had time to coat that particular portion of the lead, and so effectually prevent action with production of solid oxysalt. The supernatant water yielded slight evidence of containing nitrite, but there was no appreciable quantity of lead dissolved. The production of even a very small quantity of solid white lead-salt shows, however, what the action would be were there no " obstruction " present.

Experiment LXXIV.—New River water with 15 drops of an old rose water, which itself acted powerfully on lead, added to the five ounces, and lead as before.

After 24 hours there had been a slight action represented by two white patches on the lead near where the pieces touched the glass, and a white streak on one of the pieces of lead. Here, as in the last experiment, the production of a little white lead-salt at certain spots took place before the carbonate had time to form and cover the lead with its protective coat.

Experiment LXXV.—New River water boiled for half-an-hour, allowed to get cold and filtered, then put in jar with lead as before.

After 72 hours there had been no apparent action, but the water contained $\frac{1}{60}$ grain per gallon of lead dissolved. The lead removed from the water and allowed to dry in the air was seen to be covered with white bloom-like fur instead of the iridescent film as in the experiment with plain unboiled water. In another experiment with boiled New River water there was a considerable production of solid white curdy lead-salt, on putting lead into the water.

Experiment LXXVI.—Boiled New River water, as in last experiment, but the lead was allowed to stay in it for seven days. A portion of the water was then decanted into a clean beaker, and a piece of clean lead put into it.

Action began immediately, and in 30 seconds clouds of white lead compound were forming about the lead and falling to the bottom of the vessel. The compound was in a fine state of division. In five minutes it had given the water a very considerable degree of opalescence.

After 24 hours the action seemed to have come to an end, or, if further action was occurring, it was slow. The compound produced had subsided, the supernatant water remaining clear. The lead, as it stood in the water, was seen to be coated with a white fur. The water gave a plentiful reaction for nitrites, and had a chlorous odour. A piece of lead being removed from the water and sulphuric acid dropped upon it, it emitted an odour, which may have been mixed, but in which the nitrous gas was in the ascendant.

After 48 hours, as it was questionable whether any further action was proceeding, or whether the lead was completely protected by a layer of oxysalt on its surface, the supernatant water was removed with a pipette, and placed in another beaker with a clean piece of lead. Action occurred with production of more white lead-compound, which was of rather a curdy appearance; after another change of lead, however, scaly crystals of oxyhydrate of lead were produced in considerable quantity and continuously.

Experiment LXXVII.—Plain New River water placed in a small beaker with a piece of clean lead pipe. The volume of water was about two ounces, and the piece of lead pipe, about $1\frac{1}{4}$ inch long, offered about eight square inches of lead surface to the action of the water. Owing to the frequent change of lead, perhaps, a fifth of the water was wasted before the end of the experiment.

The lead was changed repeatedly at intervals of two hours or longer, clean bright lead being constantly put in the place of the tarnished lead which was removed.

For the first 15 changes of lead or so, the surface of the metal was covered with iridescent film, which, however, got plainly thinner in the later changes of lead.

Afterwards the lead was covered with white bloom-like fur instead of the more closely-fitting film, at first half-film and half-fur. This white fur was easily rubbed off with a duster. To see either the fur or the film the lead must be allowed to dry in the air, as it cannot be well seen when the lead is wet.

Ultimately, after many changes, the whole of the obstruction was removed, and there was a continuous production of lead compound, which fell off the lead as produced.

Thus in these experiments with a hard water, we find that normally the water has practically no action on lead, that is to say, the action is prevented by the carbonate contained in the water. When most or all of the carbonate is removed, as by boiling the water, the nitrate in the water has a better chance of acting on the lead; but there still remains in the water the sulphate of calcium, which, covering the lead with a coat of slightly soluble basic sulphate, still forms obstruction to the formation of oxyhydrate. Reference may here be made to Experiment XXXVIII., in which sulphate of calcium was added to distilled water previous to its being placed in contact with lead. Whereas the carbonate forms an iridescent film upon the lead, the sulphate forms a less smooth, white bloom-like fur easily rubbed off. When lead has been in the water long enough for all the sulphuric radicle present to attach itself to the surface of the lead, clean metal being substituted for that which is thus coated, no further obstruction exists, and the nitrate of calcium is very rapidly reduced, clouds of white lead-salt appearing in the water as the result of the appropriation of the oxygen of the nitrate by the lead with formation of oxide. Boiling the water is a rapid method of removing the carbonate of calcium, but it can also all be removed, however hard the water, when a sufficient surface of clean lead is placed in contact with the water. Anyone who has sufficient patience may prove this, as in the last experiment, which is instructive in regard to the different coats seen to be formed upon the lead.

SUMMARY.

The results obtained may now be summarized. We have satisfied ourselves that the action of water on lead is primarily an oxidizing action, and that the product in the first instance has the form of oxide of lead. Where the action is exerted in waters which do not possess the power of dissolving the oxide, the latter, together with the elements of water, forms a colourless crystalline oxyhydrate of lead very slightly soluble or insoluble in pure water. The production of this oxyhydrate of lead in such waters is continuous when free access of air is allowed to the surface of the water, and depends upon the presence of nitrate, nitrite, or an oxide of nitrogen in some other combination than as nitrate or nitrite, which is repeatedly reduced by the lead and reoxidized by the oxygen of the air, thus acting as an oxygen carrier between the air and the lead. It is further probable that the presence of chlorine in a water, as chloride, aids in the oxidation of the lead, when it exists along with nitrate, etc. We have evidence that a very minute quantity of nitrate or other form of nitrogen oxide is sufficient to set up the action of water on lead and cause its continuance, and from the nature of its origin, all waters contain, or are liable to contain this cause of action.

We have seen that the crystalline oxyhydrate of lead, produced by action of water on lead in the above manner, is more or less freely soluble in all the more commonly occurring acids, also, to a much more insignificant degree, in solutions of various salts, prominent amongst which are the salts of ammonia and particularly nitrate of ammonia. The power exhibited by various waters, and particularly by waters of acid reaction, of taking up lead into solution when they are placed in contact with the metal, is thus easily explained. For, although the acid contained in a water may have no power to dissolve metallic lead, the water contains, besides acid, the "cause of action" in the form of nitrogen oxide, that has the power of producing oxide of lead. The latter compound combines with the acid present, forming a salt of lead which is soluble in water. The presence of salts of other bases in a water that is acting on metallic lead with production of oxide of lead, also leads to the formation of other salts of lead, which often are more soluble in the water than the crystalline oxide and hydrate of lead itself, and thus waters which are not acid come to contain lead in solution. Natural waters which are not of acid reaction are never likely to contain so much lead in solution as those which do contain a free acid. It is most important to remember, however, in this connection, that it is in neutral or very slightly alkaline waters that oxidation of lead occurs with greatest rapidity, and that the insoluble oxyhydrate of lead, which is produced by such waters and which becomes so easily detached from the surface of the metal where it is produced, may cause an infinitely greater pollution of the water than any lead that may be actually dissolved. Let it be supposed that the action with production of solid oxyhydrate of lead is going on in a lead service-pipe during the night, or during a number of consecutive hours when no water is drawn, when the tap is turned the solid lead-salt will be swept out with the stream, and huge quantities of lead existing in a state of suspension may be unconsciously swallowed with such water.

It has sometimes been observed that water will act upon a new lead pipe and not upon an old one. The old pipe is probably coated with a protective covering which can only be dissolved off by an acid. In Experiment XXVIII. we found that, after clean lead had been in contact with a hard water and had thereby become coated with a protective film, a distilled water which acted on clean lead could produce no effect upon this coated lead. In the case of a very old lead pipe that has been a long time dry, the metal may be coated with dehydrated oxide of lead, which is not so easily dissolved even by an acid water. With a new lead pipe some action might be expected even in a tolerably hard water, because the pipe offers such a large surface in proportion to the volume of water it contains, that at first filling the carbonate present may be insufficient to everywhere cover the lead, and production of oxyhydrate will be the consequence.

With acid water it has to be remembered that the action is practically the same as in neutral or faintly alkaline waters. In both it is an oxidizing action, but the oxide is soluble in the acid. Although in the acid water the oxide of lead is dissolved as fast as produced, until the acid is neutralized, the major portion of the lead at first got into solution by this means is liable in the end to be deposited, being rendered less soluble by combination with a further quantity of oxide, the end-product, when a sufficient supply of oxygen is at hand, being a salt of high basicity which is but slightly soluble.

In regard to heat, the rate of action is much greater at 120° F. than at common temperature, and, no doubt, up to that point, or possibly up to a slightly higher degree, the rate of action increases with temperature, but at temperatures approaching the boiling point a continuation of action is prevented :—1, by liability to the production of an alkaline obstruction in the water, which neutralizes any acid present, and covers the lead with a protective film ; and, 2, by reason of free oxygen being driven out and kept out of the water.

In regard to hard waters, it is well to keep in mind that they are much more liable to exert an action on lead after their "temporary hardness" has been removed by boiling.

In regard to the nature of the acid in naturally acid waters, there has been much controversy. The acidity is so slight as to render it impossible of exact measurement, and as, in many instances, it cannot be concentrated by evaporation in glass or glazed porcelain vessels, simply for the reason that the acidity is neutralized or lost on boiling, it is difficult to prove its exact nature and composition. Naturally acid waters no doubt exist in which the acidity is so great as to allow of concentration by evaporation, especially if the evaporation be performed in platinum vessels, in which case the difficulty of giving the acid a name must be in great measure removed. The supply of the naturally acid waters used in the foregoing experiments was not sufficiently large for any to be used in direct experiments upon the nature of the acid present, but the author has a strong inclination to the opinion that the acidity is due to nitric and carbonic acids; in waters that exhibit a decided acidity to cochineal it will, of course, be mainly nitric. Quite a small quantity of free carbonic acid is appreciable to litmus, though the lead-dissolving power of such a quantity will be but slight. There is much to be said in favour of the acid being nitric acid, and something to be said against its being an organic acid. The author would ask, is there any organic acid known that in a proportion of much less than one grain per gallon will give a decided and *permanent* acidity such as that possessed by Huddersfield water? Everybody who has had the handling of weak dilutions of the common organic acids—acetic, tartaric, citric, malic—must have noticed that in such liquids fungoid growths invariably develop in the course of a few days; this is particularly well seen with acetic acid. Why do not these growths occur in Huddersfield water if the acid in it be acetic? In regard to other organic acids that have been mentioned as likely to give the acidity to these waters—ulmic, humic, &c.—very little appears to be known as to their properties and composition; in fact, at present they appear to be little better than names. These acids are, however, described in books as having a weak acidity. It is certain that the acid in Huddersfield water has a very powerful acidity. Rain-water often has, or is capable of developing, a decided acidity, which is quite equal to the most acid sample of Huddersfield water obtained, if, indeed, it does not exceed it. What is the usual reaction of the rain-water in those districts where the water is found to be acid in the brooks and reservoirs? If the rain-water be acid, it would appear to be quite unnecessary to seek further for the origin of the acid in the water supply, though it is quite possible to conceive that the acid of the rain-water may be augmented after its fall by decomposition and oxidation of nitrogenous material, not of necessity derived from peat or humus. The idea is surely feasible that if rain-water, after it has fallen to the earth, meets with no alkaline carbonate, by solution of which its reaction would become alkaline, its reaction will be, or will shortly become, acid. The acids it is most natural to suppose will be developed in it are nitric and carbonic. Again, these waters which act on lead undoubtedly all contain nitrate. It is easy enough to satisfy one's self on that point by an examination of the fur on a piece of lead that has been exposed to their action. Therefore, if the water contain any inorganic acid, there is a likelihood of it being nitric acid, at least in part.

Lastly, in regard to the prevention of the action of water on lead, we have seen that the introduction of an alkaline carbonate into a water prevents the action that would otherwise occur, and that it is also prevented in those waters which naturally contain carbonate of lime. In an alkaline water phosphate has also power of giving the lead a covering which protects it, but the action of water does not appear to be so promptly stopped by phosphate as by carbonate. From a practical point of view, too, the addition to a water of phosphate for the purpose of preventing action on lead is not likely to answer, inasmuch as it would be useless to add it to an acid water, because it cannot protect the lead in an acid solution, and has no power of neutralizing the acid, and it is chiefly in acid waters that pollution by lead occurs. With silicate better results were expected than those obtained. Silica, when present in an acid water, appears to have some power of covering the lead with a protective coat, but this coat seems to be formed too slowly and too imperfectly to prevent lead being taken into solution. When the water is alkaline it is questionable whether the presence of silica is of any advantage. The satisfactory effects said to have been obtained by passing a lead-dissolving water over flints are more likely to have been due to the neutralization of the acid in the water and solution of a small quantity of carbonate derived from the flints than from solution of silica.

Thus at present the best answer to the question of how the action of water on lead is to be prevented, lies in the addition of an alkaline carbonate to the water. The most natural and least objectionable carbonate for the purpose is carbonate of lime, a solution of which that has a constant strength of two grains in the gallon being amply sufficient for perfect protection of the lead. In fact it will probably be found that when a lead pipe has already become well coated by exposure to the action of a water containing as much as or more than two grains of carbonate of lime per gallon, a much weaker solution than this will suffice to prevent the removal of the protective coat, provided that the water does not at the same time contain considerable excess of carbonic acid gas over that which is required to keep the calcium carbonate in solution. So far there seems to have been some difficulty in getting so much as two grains per gallon of this carbonate into solution, but this difficulty will probably be overcome when a little more thought has been given to the question. For its solution in water carbonate of lime depends upon the presence of free carbonic acid. Experiments might be made with various limestones with the object of determining whether one is more soluble in water than another. Possibly the less compact native carbonates of lime are more readily taken up by water than the harder varieties. There may be an objection to the most friable varieties, such as the chalks, on account of the turbidity which an excess would cause in the water; this, however, must depend upon how and where, and in what quantity, the chalk is applied. It is not unlikely that a considerable and important difference might be found to exist between one variety of limestone and another in regard to ability for absorbing carbonic acid gas from the air when exposed in a dry state, and the discovery of any such difference might lead to the solution of the difficulty. The greater the natural acidity of a lead-dissolving water, the greater should be its power of dissolving carbonate of lime, because free carbonic acid will be the result of the neutralization of the acid in the water by a portion of the carbonate, and this carbonic acid will be set free in proportion to the acid which is present to displace it. The best place to apply the limestone to the water must be, not at the outlet of a reservoir, but at intervals in the streams which supply the water, beginning at their most remote points of origin. Another method of getting sufficient carbonate into the water, which must be practicable in many places, though of course necessitating some outlay, will be to obtain a hard spring or well water, and mix it in suitable proportion with the soft lead-dissolving surface water. The quantity of hard water required to attain the object would not be great in proportion to the soft water. In the experiment recorded it will be remembered that one part of New River water to twenty parts of Mirfield water was found to be more than enough to prevent action upon lead.

In regard to the practical prevention of the action of water upon lead pipes, the author does not pretend to have exhausted the subject. He trusts a perusal of this essay may lend some aid to other gentlemen who are at present engaged upon the same pursuit, and is sanguine that an easily-applied and thoroughly efficient method will at length be found to altogether avert the danger arising from lead in drinking-water.

A READY METHOD OF DETECTING AND ESTIMATING MINUTE TRACES OF LEAD IN DRINKING-WATER.

The usual method of testing for lead in water consists in precipitating it with sulphuretted hydrogen or sulphide of ammonium. The lead, whether in acid or alkaline solution, is thrown out on the addition of either of these re-agents as sulphide of lead, and the intense brown colour of this salt renders it readily perceptible. In testing for lead in drinking-water, it is necessary to acidulate the water with hydrochloric acid as a preliminary proceeding, the object being to prevent the precipitation of iron, which is very likely to be present along with lead, and which is also precipitated in alkaline solution as a dark sulphide. The limit of the test is reached when the strength of the solution is less than one part of lead in 700,000 of water, or $\frac{1}{10}$ grain of lead per gallon. To appreciate with certainty smaller quantities of lead than this requires concentration of the solution by evaporation, a process which is ordinarily not resorted to. As it is important that lead should be discovered if present, even though in smaller proportion than $\frac{1}{10}$ grain per gallon, and as even this quantity may escape detection in the hands of an unpractised operator, a modification of the test which readily leads to the certain discovery of lead in exceedingly dilute solutions, should be worth attention. Whatever be the degree of dilution of the solution of lead, there is no doubt that the sulphide of lead is formed on addition of sulphide of hydrogen or ammonium, although the consequent darkening in the water may be too slight to be observed by a person of ordinary powers of vision. Hence the idea arose of endeavouring to bring the precipitate into a small compass by adding some insoluble white powder, which, in being precipitated itself, should collect and bring down the sulphide of lead along with it, the presence and quantity of the lead being declared by the degree of colour imparted to the white powder. Of the powders tried, dried sulphate of barium was found to answer by far the best. When this substance is shaken with water in a test-tube and the tube then placed in the test-tube rack and allowed to stand, the subsidence of the sulphate of barium takes place in two well-defined layers. The lower layer is formed by the more aggregate particles of the sulphate, and comes down very rapidly. The upper layer is finer and takes longer to subside.

It is in this second or upper layer that the sulphide of lead is contained if present in the water, and the first or lower layer being white and sharply defined from the upper layer, allows of a comparison which renders the test very delicate. The colour imparted varies from the palest Indian grey or buff to darkest brown. In half an ounce of water in a six-inch test-tube lead equivalent to one part in 14,000,000, or $\frac{1}{200}$ of a grain per gallon, is detected with certainty by this means, and if there were any practical advantage in detecting much smaller quantities, it could doubtless be done by using a longer tube. Comparisons of precipitates obtained from waters containing lead may be made with those from a water to which a known quantity of acetate of lead has been added, and a fair estimate of the quantity of lead present can be thus arrived at. The following is the best method of applying the test:—Take a narrow test-tube, that which is six inches long and half an inch in diameter answers well, put into it half an ounce of the water and one drop of dilute hydrochloric acid. Pass washed H_2S through it, or add one drachm of strong, freshly prepared sulphuretted hydrogen water, and add half a grain of sulphate of barium. Shake and set aside. If the water be made alkaline with a drop of ammonia and the precipitate again diffused through the water by a shake, the test becomes equally delicate for iron. The sulphide of iron has a green tint, and soon becomes paler through oxidation. Precautions:—Let the quantity of hydrochloric acid that is added be limited, a very slight acidity suffices to prevent precipitation of iron, whereas much acid has a decided tendency to dissolve small quantities of PbS. The quantity of the precipitate is different for the same quantity of lead when Am_2S and H_2S are used, due no doubt to the large amount of sulphur precipitated from the former. So that in comparative testing use either one re-agent or the other throughout. Use a very small quantity of $Ba\,SO_4$. In comparative experiments always the same amount. Half a grain is a convenient quantity for a small test-tube. Use sulphate of barium powder, and do not attempt to precipitate it in the water by addition of nitrate or chloride of barium and sulphuric acid or a soluble sulphate, because in that case the barium comes down all in an equal state of division and forms one equal layer, and the comparison of a contiguous upper and lower layer, upon which the delicacy of the test depends, is not obtained.

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